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DEVELOPMENT OF IMPROVED ALKALIZED ALUMINA FOR SO_2 CONTROL

FINAL REPORT

BY

W. 3. BRIGGS, E. EICHHORN, AND P. K. MAHER

COVERING THE PERIOD
JUNE 15, 1967 THROUGH SEPTEMBER 15, 1969

CONTRACT NO. PH-86-67-129 WITH
NATIONAL AIR POLLUTION CONTROL ADMINISTRATION
PUBLIC HEALTH SERVICE
DEPARTMENT OF HEALTH, EDUCATION & WELFARE

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A final, summary report of studies on the use of activated alkalized alumina for the removal of SO_2 from flue gases. Investigation of this process in the laboratory and pilot plant resulted in the following questions regarding the performance characteristics, method and cost of manufacture of alkalized alumina: 1. maximization of sorption rate and capacity, 2. maximization of regeneration rate, 3. minimization of regeneration cost with regard to temperature and reducing gas used, 4. Improving of attrition resistance of the sorbent, 5. Development of a low cost manufacturing procedure, These questions are also the objectives of the program.

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Flue gases
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Manufacturing costs

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TABLE OF CONTENTS

	Page
PREFACE	1
I. Objectives	1
II. Summary of Results and Conclusions	1
Section A. Initial Investigations	5
I-A. Introduction	6
II-A. Details	6
A] Methods of Synthesis	6
1. Modification of Bureau of Mines Procedure	6
2. Reactions of $NaAlO_2$ with $NaHCO_3$	7
3. Reaction of $NaAlO_2$ with CO_2	7
(Table I) Evaluation of Alkalized Alumina from Reaction of $NaAlO_2$ & CO_2	8
B] Forming Methods	9
1. Day Company Pony Mixer	9
2. Pan Granulator	9
3. Pellet Mill & Continuous Pilling Extruder	9
4. Auger Type Extruder	9
(Table II) Attrition Resistance vs. Conditioning Time, % Loss	10
C] Sorbent Production Costs	10
1. Alternate Raw Materials	10
(a) Bienstock Process	10
(b) Sodium Aluminate-Sodium Bicarbonate Process	11
(c) Sodium Aluminate-Carbon Dioxide Process	11
2. Extrapolated Commercial Plant Costs	12
(Figure 1) Process Flow Diagram	13
(Figure 2) Alkalized Alumina Plant Layout	14

		Page
	(Table III) Estimated Capital Cost 50T/S.D.	15
	(Table IV) Alkalized Alumina Order of Magnitude Price 45 Ton/ Calendar Day Plant	16
D	Sorption & Regeneration Studies	12
	1. Effect of Additives on Sorption and Regeneration	17
	(Figure 3) Schematic of Sorption Unit	18
	(Figure 4) Schematic of Regeneration Unit	19
	(Table V) Evaluation of Grace #1 after Activation at 1100°F	21
	(Table VI) Evaluation of Grace #1 vs. Spray Dried Alkalized Alumina	22
	(Table VII) Evaluation of the Effect of Additives on Sorption and Regeneration	24
	2. Study of Regeneration Parameter	23
	(Figure 5) Effect of Promoters on Hydrogen Regeneration	25
	(Table VIII) Summary of Regeneration Study	26
E	Endurance Testing of Formed Product	27
	1. Cyclic Aging Test Development	28
	(a) Introduction	28
	(b) Results	28
	(Table IX) Steam & Thermal Aging Data	29
	(c) Discussion	28
	2. Multicycle Test	30
	(Table X) Standard Sorption-Regeneration Cycle	32
	(Figure 6) Extended Aging - Grace #1	33

		Page
F	Chemistry of the Alkalized Alumina Process	31
	1. Activation Atmosphere	31
	2. SO_2 Concentration & Space Velocity	34
	3. Oxygen	34
	4. Temperature	34
	(Table XI) Sorption Regeneration Characteristics of Grace #1 Alkalized Alumina Powder	35
	(Table XII) Material Characteristics Before & After High Temperature Operation	35
	5. Effect of CO_2 on Sorption	34
	(Table XIII) Effects of CO_2 on Sorption	37
	6. Effect of NO_x on Sorption	36
	(Table XIV) Flue Gas Composition vs. Attrition Resistance	38
	7. Effect of Poisons	39
	8. Effect of CO_2 on Regeneration	39
	(Table XV) Effect of CO_2 on Regeneration	40
G	Portable Aging Units	39
Section B.	Screening New Sorbents for Improved Attrition Resistance	41
I-B.	Introduction	42
	(Figure 1) % Loss vs. Crystallite Size for Grace #2 Alkalized Alumina in Laboratory Tests	43
II-B.	Details	45
A	Methods of Sample Preparation	45
	1. Binder Incorporation & Beading Technique	45
	2. Impregnation	45
B	Evaluation for Sorption Efficiency and Attrition Resistance	46
	1. Single Cycle Screening Test	47

		Page
	2. Multicycle Aging Test	47
	(Table I) Comparison of Results from Laboratory & Field Units	48
	3. Process Variables	47
	(a) Sorption Temperature	47
	(b) Regeneration	49
	(c) Activation	49
	(Table II) Effects of Sorption Temp. on Attrition Resistance of Grace #2	50
	(Table III) Effects of Activation Condition on Attrition Prior to Sorption	51
	(Table IV) Evaluation of Kaolin Binders and Effect of Heat Treatment on Attrition	52
III-B.	Conclusions and Recommendations	53
	(Table V) Evaluation of Alkalized Alumina Binders	54
	(Table VI) Evaluation of Carriers Impregnated with Sodium Aluminate	55
	(Table VII) Composition and Process Recommended for Further Development	56
Section C.	Laboratory and Pilot Plant Production of Attrition Resistant Sorbents	57
I-C.	Introduction	58
II-C.	Details	58
	A] Laboratory Preparations	58
	(Table I) Summary of Results on Bound and Formed Alkalized Alumina	59
	1. Precipitation of Dawsonite in the Presence of Binders	58
	2. Meta-Kaolin Preparation	60
	(Table II) Physical Evaluation of Insitu Binder Preparation	62

Page

(Table III) Physical Evaluation of Meta-kaolin Binder Dry Blended 63

(Tabel IV) Sorption and Attrition Evaluation of Various Samples 64

B. Pilot Plant Preparations 61

III-C. Conclusions and Recommendations 65

(Table V) Evaluation of Beads Made Using the Marumerizer 66

APPENDIX - A. Modified Air Jet Attrition Test 69

B. Sophisticated 5 Module Field Test Unit 75

C. Organization Chart 79

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P R E F A C E

The work reported here covers the total period from June 15, 1967 through September 15, 1969 on Contract No. PH-86-67-129. Two comprehensive reports have already been issued (May 15, 1968 and July 15, 1969) which detailed all of the work done during those periods. It is the object of the present report to summarize in Section A the salient features of the work reported in full earlier and to detail in Sections B and C the work done from May 15, 1969 through September 15, 1969.

I. Objectives

The use of activated alkalized alumina for the removal of sulfur dioxide from flue gases had been under investigation at the Bureau of Mines, Bruceton, Pennsylvania, station both in the laboratory and pilot plant for some time. While the initial technical feasibility of the process appeared promising, a number of questions regarding the performance characteristics, method and cost of manufacture of alkalized alumina remained.

Specifically, information was required on the following topics, which form the objectives of the program.

- Maximization of sorption rate and capacity
- Maximization of regeneration rate
- Minimization of regeneration cost with regard to temperature and reducing gas used
- Improving of attrition resistance of the sorbent
- Development of a low cost manufacturing procedure

II. Summary of Results and Conclusions

The discovery of the adverse effect of NO_x on attrition resistance materially increased the difficulty of producing a suitable sorbent. Despite this we believe the objectives of our study have been met. A ceramic binder system was developed which gave a sorbent with less than 5% air jet attrition after a 46 cycle field test using power plant stack gas. Under these same conditions the best sorbent

without binder is virtually destroyed. Although the drying and heat treating steps were done in the laboratory, the forming and conditioning procedures used to produce this improved sorbent were carried out using pilot plant equipment.

In the absence of definitive plant performance, the practical utility of our improved sorbent remains unknown.

The main results of the work done are tabulated below:

1. Many of the problems associated with the process and the equipment required for the commercial preparation of alkalized alumina by various methods were resolved at the pilot plant level. The most practical commercial equipment was determined for filtration, washing, drying and forming of the alkalized alumina.

2. New products, showing significant improvements in SO_2 sorption rates, regeneration rates and attrition resistance, resulted from the pilot plant and laboratory studies.

3. Laboratory and pilot plant studies showed that a high quality dawsonite can be prepared by the reaction of CO_2 and sodium aluminate.

4. The raw material costs were defined more precisely for preparing alkalized alumina by several processes. The raw materials for the CO_2 - sodium aluminate process were the cheapest, $0.041/lb. of dawsonite product. The cost of the raw materials used in the Bureau of Mines process was $0.078/lb. of product.

5. A detailed preliminary estimate of the capital and operating costs of a 50 T/Stream Day plant for the CO_2 - aluminate process based on laboratory and pilot plant data indicated a plant cost of $4,800,000 and a selling price of approximately $0.20/lb.

6. Standard alkalized alumina was characterized using up-to-date analytical techniques. These included the surface properties, porous structure, x-ray analysis, chemical analysis, and rates of sorption

of SO_2 and regeneration. Dawsonite, the activated, spent and regenerated materials were characterized by these procedures.

7. Sulfur dioxide sorption rate studies on formed bead products showed clearly that initial rates increase with increase in surface area and pore volume of the sorbent.

8. The best promoter found for increasing the sulfur dioxide sorption rate was copper at a concentration of about 1%.

9. Extensive studies were completed on the effect of promoters on the regeneration rate of spent alkalized alumina. The data showed the small concentrations (0.5 to 1.0%) of a hydrogen activating metal such as iron, or nickel, or a metal oxide such as vanadium oxide were required to obtain rapid regeneration rates.

10. Regeneration rates using ethane or propane were found to be superior to those using hydrogen, but possible long term effects due to coke buildup were not evaluated.

11. Laboratory studies showed that low partial pressures of steam should be maintained in the regeneration at all times. Unit design, for removal of SO_2, using alkalized alumina should minimize hydrothermal aging of the sorbent during the regeneration step.

12. A reproducible laboratory cyclic aging test was developed based on the data obtained from the hydrothermal treatment of alkalized alumina.

13. Investigations of various factors on the SO_2 sorption rate using real stack gas showed that the presence of nitric oxide in the gas had the most significant effect. Nitric oxide increased the rate of SO_2 sorption but produced poor attrition resistance.

14. Arsenic compounds in the stack gas and carbon monoxide in the regenerating gas adversely affected the regeneration rate. An increase in regeneration rate was observed when carbon dioxide was present in the regenerating gas.

15. Two portable field testing units were constructed and used for sorbent evaluation at the Dickerson station of the Potomac Electric Power Company and at the Crane station of the Baltimore Gas and Electric Company.

16. A comprehensive study of the attrition problem resulted in the discovery of several binder systems which showed much improved attrition resistance. The following systems were the best found.

    - 23% Kaolin, 2% Na silicate, 75% Dawsonite
    - 25% Meta-kaolin, 75% Dawsonite

17. A larger, more sophisticated, thin bed sorbent test unit was constructed for future use in testing new sorbents or modified processes.

SECTION A

INITIAL INVESTIGATIONS

I-A. Introduction

Prior to the assumption of the present contractual obligation, a 6000 lb. quantity of alkalized alumina was prepared by W. R. Grace for the U. S. Bureau of Mines. This product was made according to their specifications, using a mole ratio of Na_2CO_3 to $Al_2(SO_4)_3$ of 3.6, in which $Al_2(SO_4)_3$ solution is added to the Na_2CO_3 solution forming the precipitate of alkalized alumina. This material when pan granulated and tray dried yielded the product called Grace #1. This was the initial standard against which improvements were measured.

The object of this part of the investigation was to improve on the method of producing alkalized alumina from the point of view of:

- Cost
- Physical Properties (Attrition Resistance)
- Sorption Characteristics

In order to satisfy these objectives the studies were directed toward improved methods of dawsonite synthesis and development of more effective forming techniques.

II-A. Details

A. Methods of Synthesis

1. Modifications of Bureau of Mines Procedure

Spray drying of the washed product was used as opposed to the tray drying procedure for Grace #1. This resulted in a product having increased pore volume and surface area. Modification of the forming technique (extrusion followed by rolling) produced a product of closely controlled particle size (10 - 14 U. S. mesh), and improved attrition resistance based on the test procedures used at the time. This process (with iron oxide additive) was used to prepare the 6000 lbs. of product sent to the Bureau of Mines as Grace #2. Grace #2 also served as the reference point for attrition evaluations.

The alkalized alumina made by the reaction $NaAlO_2$ and CO_2 was as good as the standard alkalized alumina with regard to sorption and regeneration.

Although the Bureau of Mines' method of synthesis was the best defined method from the standpoint of process economics and product purity, the carbon dioxide method utilizing a high concentration of sodium aluminate solution in a continuous system was considered the most promising method of synthesis. Therefore, the process economics and plant design were prepared utilizing the carbon dioxide method of dawsonite preparation.

B| Forming Methods

Considerable effort was devoted to developing forming or beading methods. Particle shape and physical characteristics of alkalized alumina product are critical in the SO_2 dispersed-phase sorber as designed by the Bureau of Mines. Spherical particles would be the ideal shape because of potentially better attrition resistance.

The following types of forming equipment were investigated:

1. Day Company Pony Mixer

   Dawsonite was added to the mixer and water was added during mixing. Particles of the proper size could be formed but did not have the desired spherical shape.

2. Pan Granulator

   Moistened dawsonite was added to a pan granulator at a variety of moisture levels. Extensive tests failed to produce a product having the desired spherical shape and attrition resistance.

3. Pellet Mill and Continuous Pilling Extruder

   Both types of pilling equipment used a dry feed. The resulting pills had to be remoistened throughout in order to be subsequently beaded by rolling.

4. Auger Type Extruder

   This was the most satisfactory equipment tested. The

resulting spaghetti like extrudates could be cut or fed directly into a rotary drum where the extrudates broke into lengths about equal to their diameter.

With regard to the auger type extruder, it was possible to obtain bead size in the range of 8 to 20 U. S. mesh. Other factors affecting the rounding or beading of the product were the bed depth in the rotary forming drum and the total moisture content of the extrudates.

It was initially concluded that the best forming method was to use an auger type extruder and then shape the extrudates into spheres in a rotary conditioning drum. The rotary drum treatment improved the attrition resistance of the beaded product as shown in Table II.

TABLE II

ATTRITION RESISTANCE VS. CONDITIONING TIME, % LOSS

15 Min.	1 Hr.	2 Hrs.	3 Hrs.	4 Hrs.	6 Hrs.
13.0	7.4	4.0	3.3	2.3	Under 1

When the critical role of NO_x in sorbent attrition response was recognized, a ceramic type binder system was developed. However, difficulty was experienced in reproducibly preparing attrition resistant beads of this composition by the described technique. Since the problem appeared in the conditioning step, other conditioning equipment was employed, the most successful of which was a Marumerizer. Use of this equipment, details of which appear in Section C, "Laboratory and Pilot Plant Preparation of Improved Sorbents", consistently yielded beads of good attrition resistance.

C| Sorbent Production Costs

1. Alternate Raw Materials

(a) Bienstock Process

The Bienstock process can be represented by the following equation based on a fixed ratio of $2Al(OH)_3 : 3.6Na_2CO_3$:

$$2Al(OH)_3+3H_2SO_4+3.6Na_2CO_3 \longrightarrow 2NaAl(CO_3)-$$

$$(OH)_2+2.6Na_2SO_4+1.6H_2CO_3+0.4H_2SO_4+2H_2O$$

Calculating the input per pound of product and using Baltimore area costs, the raw material costs on a 100% yield basis are $.0777/# as shown below:

0.542# C-31 alumina hydrate	@ .0404=	$.0219
1.02# 100% H_2SO_4	@ .0167=	$.0170
1.33# Na_2CO_3 (reaction)	@ .0175=	$.0233
0.883# Na_2CO_3 (washing)	@ .0175=	$.0155
Per Pound of Product		$.0777

(b) Sodium Aluminate-Sodium Bicarbonate Process

The sodium aluminate-sodium bicarbonate process, using the optimum conditions, can be represented by the following equation:

$$2.6NaOH+2Al(OH)_3+4.4NaHCO_3 \longrightarrow 2NaAl$$

$$(CO_3)(OH)_2+2.4Na_2CO_3+0.2NaOH+4.4H_2O$$

By the same procedure as above the raw material costs are derived:

0.542# C-31 alumina hydrate	@ .0404=	$.0219
0.362# NaOH (100%)	@ .0330=	$.0119
1.36# $NaHCO_3$	@ .0280=	$.0381
Per Pound of Product		$.0719

(c) Sodium Aluminate-Carbon Dioxide Process

The sodium aluminate-CO_2 process was not fully delineated; however, the following equation was used for initial cost comparisons:

$$2.8NaOH+2Al(OH)_3+2.6CO_2 \longrightarrow NaAlCO_3(OH)_2+$$

$$0.4NaHCO_3+0.2Na_2CO_3+2.2H_2O$$

Using the foregoing procedure, the cost (100% yield basis) is:

0.542# C-31 alumina hydrate	@ .0404	=$.0219
0.389# 100% NaOH	@ .0330	=$.0128
0.396# CO_2	@ .0150	=$.0059
Per Pound of Product		$.0406

2. Extrapolated Commercial Plant Costs

Although the experimental program did not develop sufficient information for a rigorous evaluation, an estimate of costs was feasible. A plant design was prepared and estimated based on the following factors:

- Plant Size - 50 Tons/Stream Day with 90% operating factor.
- Product is dawsonite - $NaAlCO_3(OH)_2$ - dried, not activated.
- Battery-limits plant - located within confines of larger plant with utilities close by and supporting services available.
- Baltimore, Maryland, area used for pricing.
- Extrapolation of laboratory and pilot plant data to full scale.

A process flow sheet for the operation is given in Figure 1, and a plant layout in Figure 2. The capital cost for the plant is shown in Table III. Cost of the product is given in Table IV.

D. Sorption and Regeneration Studies

This work was divided into two areas. The first was a study of:

- The effect of additives in increasing the effective sorption capacity (rate).

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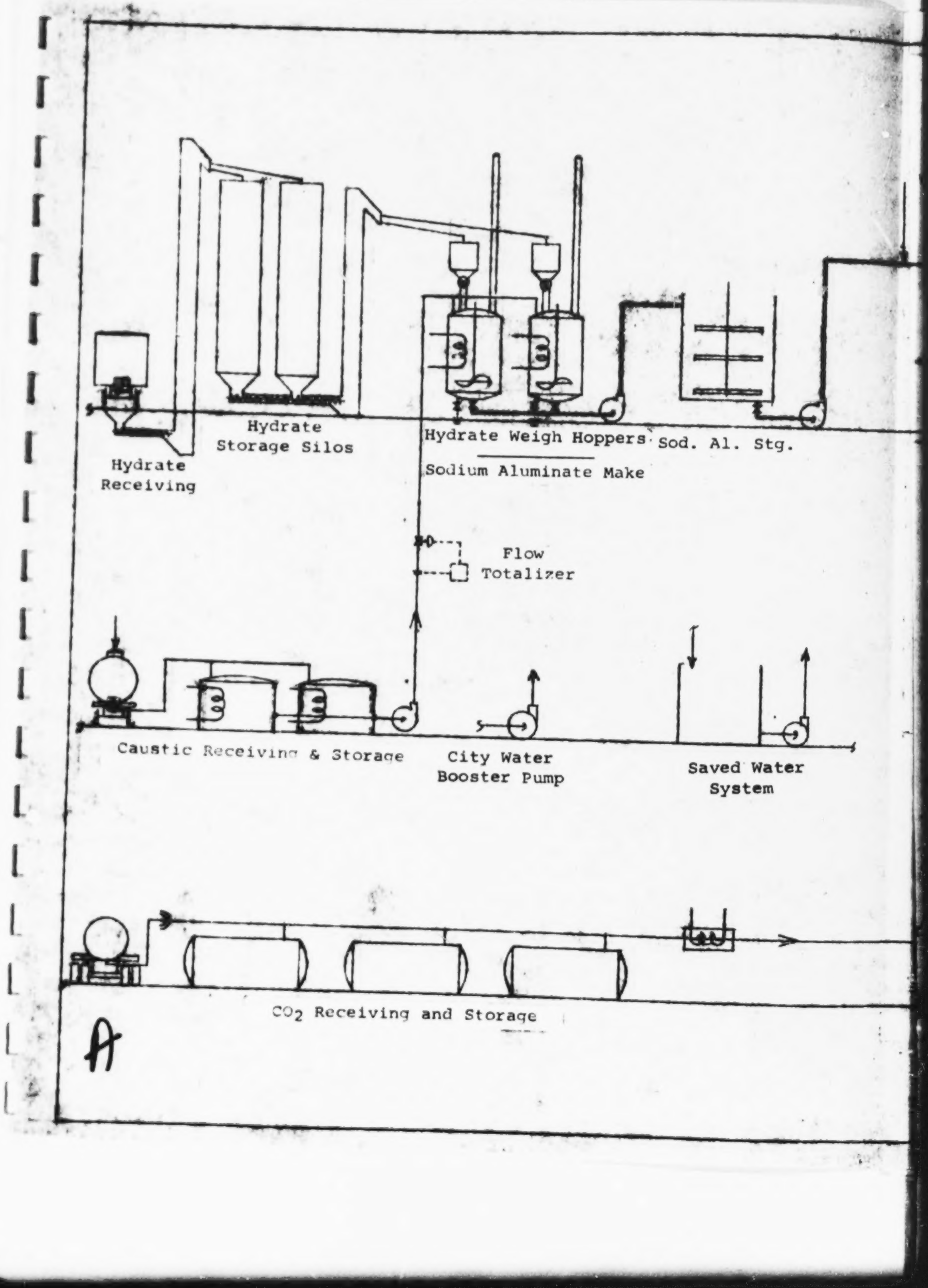
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Hydrate Weigh Hoppers
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Caustic Receiving & Storage
City Water Booster Pump
Saved Water System
CO_2 Receiving and Storage
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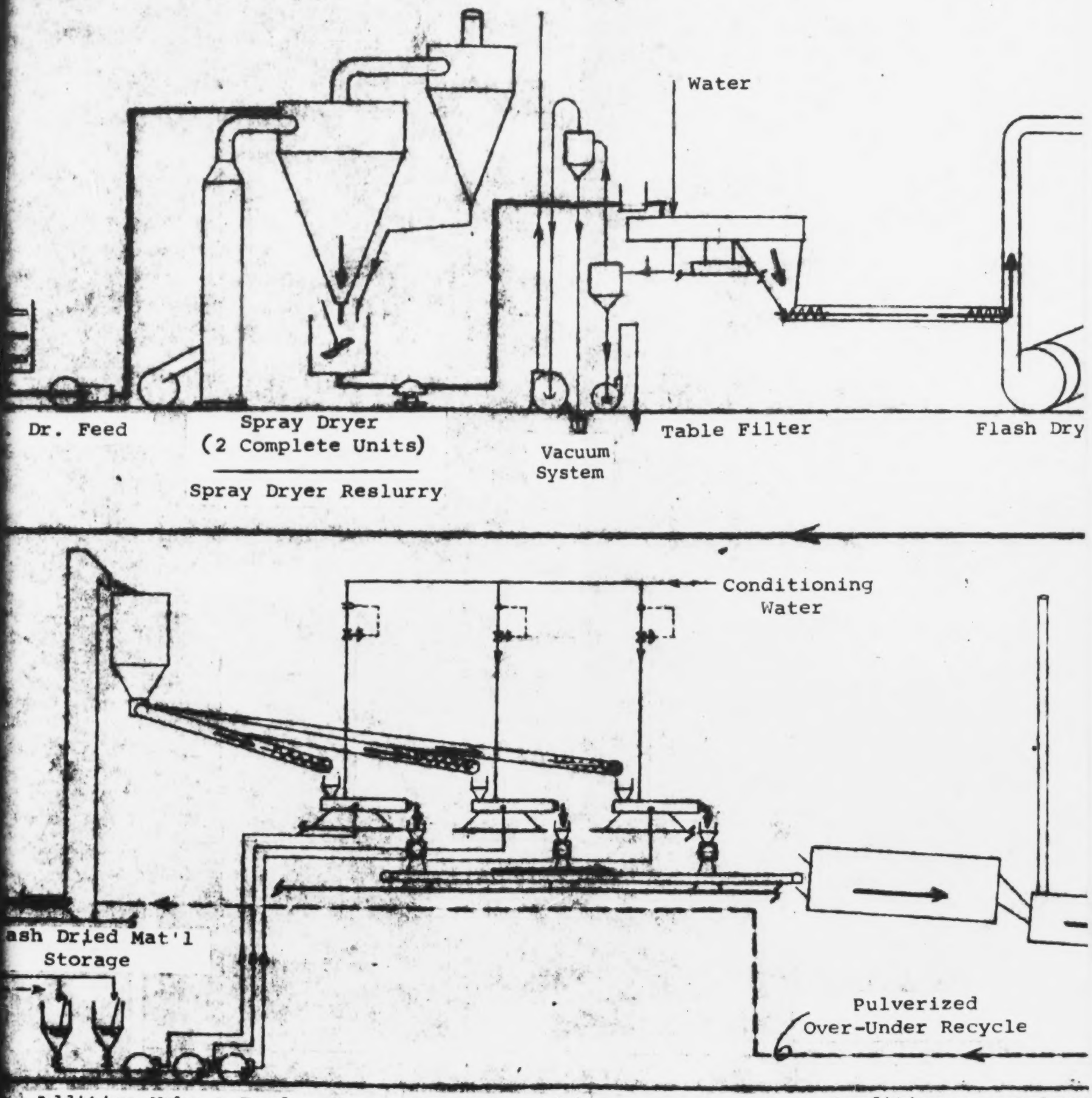
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Table Filter
Flash Dry
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Extructors (3)
Extruders (3)
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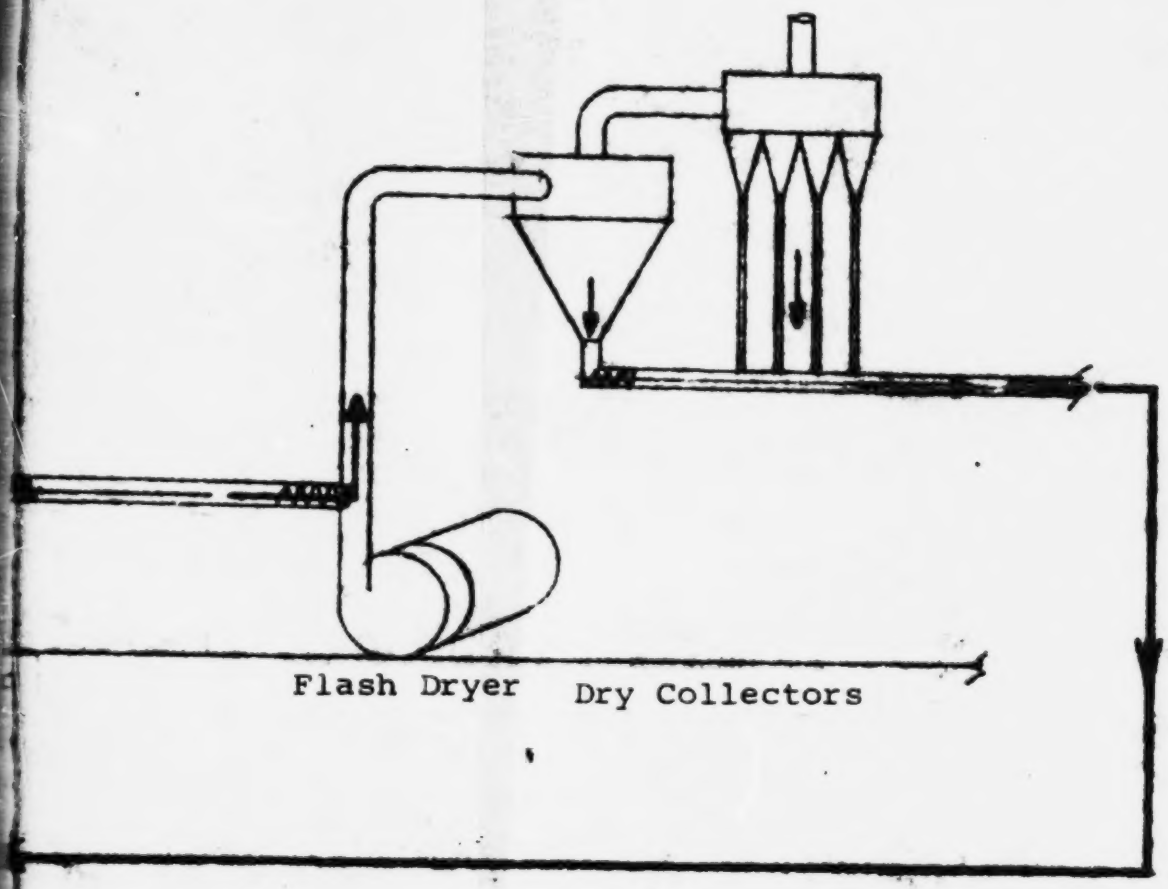
Rotary Conditioner
Rotary


Flash Dryer
Dry Collectors

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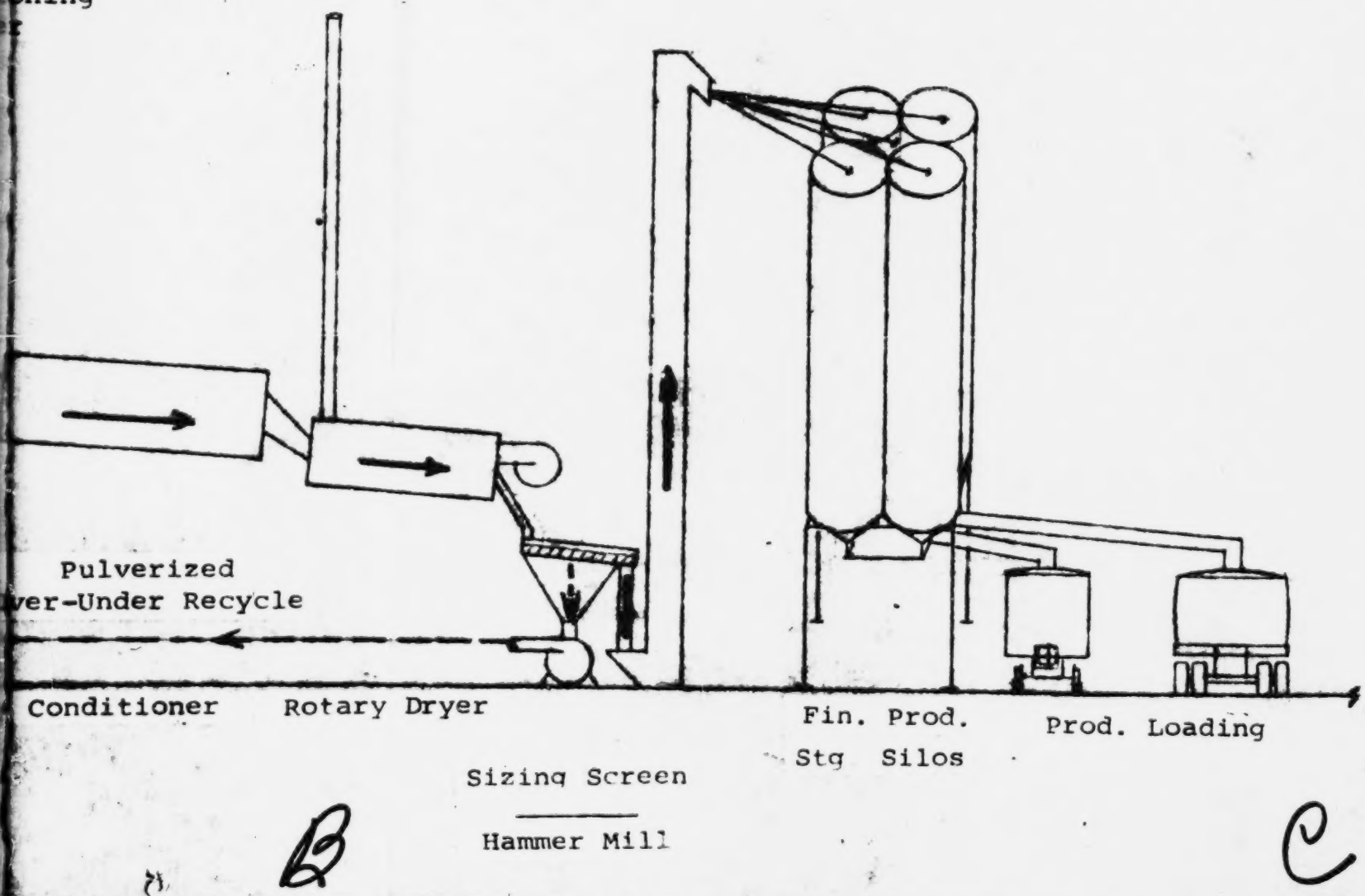
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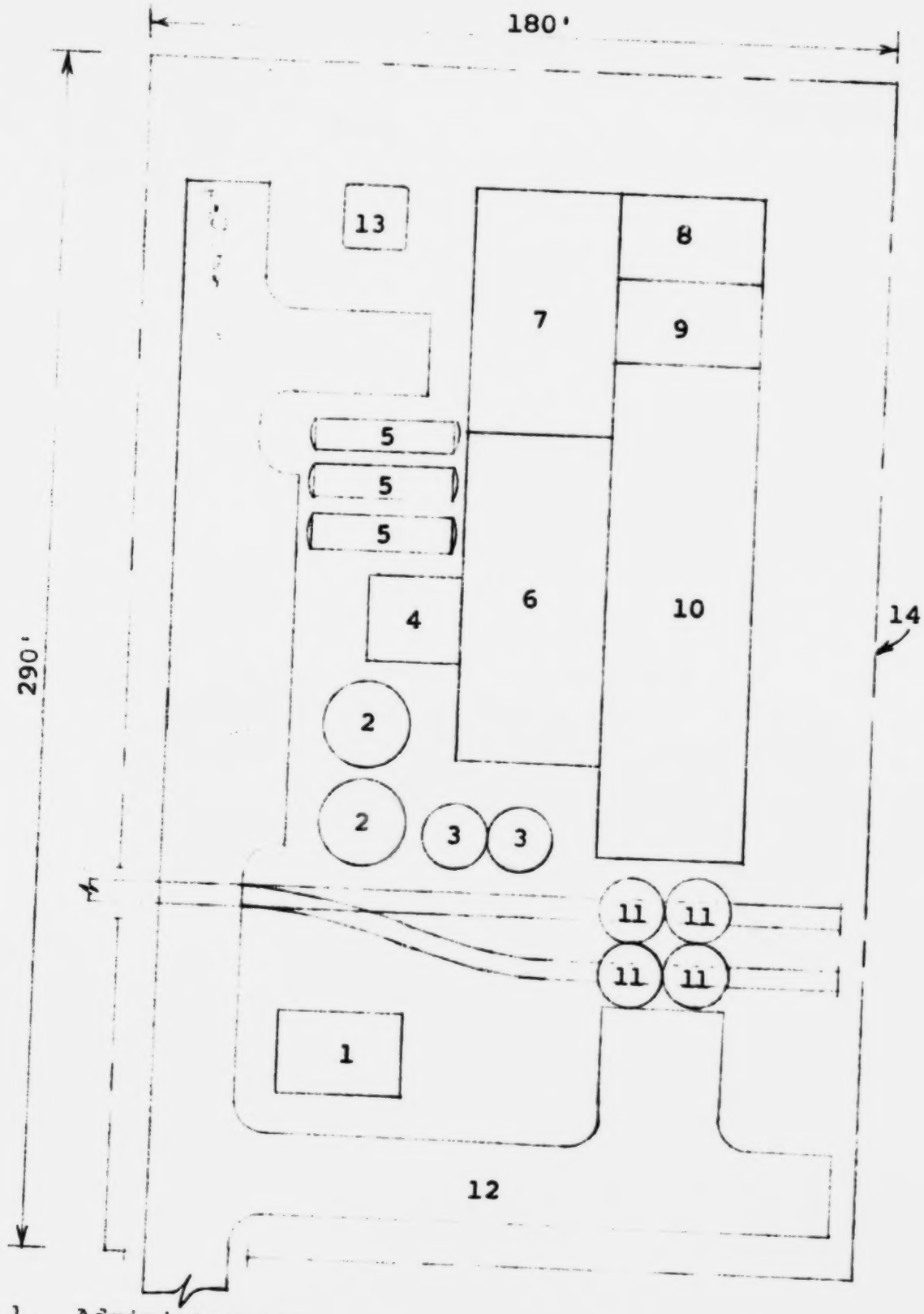
Conditioner
Rotary Dryer
Fin. Prod.
Stg Silos
Prod. Loading
Sizing Screen
Hammer Mill
B
C



Key:
1. Administration
2. 50% Na OH Tanks
3. Aluminum Hydrate Silos
4. Boiler House
5. CO_2 Tanks
6. Wet Process Area
7. Spray Dryer Area
8. Flash Dryer & Collectors Area
9. Extruder Area
10. Rotary Conditioning & Drying
11. Product Silos & Loading
12. Roads
13. Electrical Substation
14. Fence - Battery Limits

ALKALIZED ALUMINA PLANT - LAYOUT
SCALE 1" = 40'

FIG. 2

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TABLE III

ESTIMATED CAPITAL COST - 50 T/S.D.
ALKALIZED ALUMINA PLANT

Installed Equipment Costs	
Vessels, etc.	$ 298,500
Heat Exchangers, etc.	45,800
Pumps, Fans, Blowers, etc.	72,450
Screws, Elevators, etc.	71,900
Agitators	72,000
Filters	184,500
Mills, Extruders, etc.	134,000
Heaters, Spray Dryers, etc.	1,035,000
Electrical	124,600
Instrumentation	46,000
Total Installed Equipment Cost	$ 2,084,750
(Purchased Equipment Cost $1,318,450)	
Structural (10,500 sq. ft.)	$ 65,000
Concrete Foundations 231 CY	23,000
Building (10,500 sq. ft.)	250,000
Piping (45% Purchased Equipment Cost)	590,000
Utility Supplies	50,000
Railroad Trackage	15,000
Site Work	15,000
Total Direct Plant Cost	$ 3,092,750
Total Cost	$ 3,100,000
25% Contractor's Overhead & Profit	$ 750,000
Subtotal	$ 3,850,000
10% Direct Plant Cost for Engineering	$ 310,000
Subtotal	$ 4,160,000
15% Contingency	$ 640,000
Job Total	$ 4,800,000

Basis of Estimate

1. Process conditions and equipment extrapolated from bench scale work.

2. Battery-Limits manufacturing building and operation, not including shops, analytical labs, change houses, general offices, etc.

3. Based on current prices of equipment and labor in Baltimore, Md.

- The effect of additives in lowering the regeneration temperature.

- The use of less costly regenerating gases.

The second was the development of techniques for evaluating the endurance of the formed product with regard to:

- Retention of useful capacity (sorbent life).

- Attrition resistance.

1. Effect of Additives on Sorption & Regeneration

In order to evaluate the effect of additives on both sorption and regeneration, powders between 50 and 80 mesh size were used. Powders were studied as opposed to formed beads to minimize the effect of shape and size and to obtain a better picture of the true activity of the materials as sorbents.

The apparatus used to evaluate effective SO_2 capacity and equilibrium capacity is shown in Figure 3. Essentially, this consists of carrier lines to provide a synthetic flue gas having the composition in mole %: 0.3% SO_2, 12.0% CO_2, 6.0% O_2, 5.6% H_2O and 75.9% N_2, a furnace for maintaining the sorbent at a relatively high temperature and a gas chromatograph for measuring SO_2 concentrations.

Gas of the composition indicated was passed through a reaction tube, containing a constant volume of the sorbent, enclosed in the furnace maintained at 600°F.

The effluent coming from the reaction tube was monitored for SO_2 concentration by gas chromatography. The break time (t_B) was defined as the time at which the effluent gas stream reached 5% of the SO_2 found in the feed gas stream. The break capacity was defined as the quantity of SO_2 sorbed per unit weight of the reactant during this time.

The apparatus used to evaluate the regeneration rate is shown in Figure 4.

TABLE IV

ALKALIZED ALUMINA
ORDER OF MAGNITUDE PRICE
45 TON/CALENDAR DAY PLANT*

		Estimated Cost Per Pound
Raw Materials		
Aluminum Hydrate	0.68#/# @ .041	$ .028
50% Liquid Caustic Soda	0.97#/# @ .0165	.016
Carbon Dioxide	0.55#/# @ .015	.008
Iron Oxide	0.005#/#@ .1635	.001
Total		0.053
Utilities		
Natural Gas	20 C.F./#@ .0005	.010
Electricity	0.3 KWH/# @ .013	.004
Steam	3#/# @ .00076	.002
Water	5 gal/# @ .0002	.001
Total		0.017
Direct Labor		
.002 Manhours/# @ 3.10/hour		.006
Benefits		.001
Total		0.007
Supervision and Plant Services		.010
Maintenance		.007
Operating Supplies		.012
Depreciation #(10 yr. Basis)		.015
Total Factory Cost		$0.121
Selling Price		~$0.200

Note: Plant product is dawsonite $NaAlCO_3(OH)_2$ dried but not activated.

* Based on 90% operating factor, average calendar/day production is 45 ton/calender day.

- The effect of additives in lowering the regeneration temperature.

- The use of less costly regenerating gases.

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1. Effect of Additives on Sorption & Regeneration

In order to evaluate the effect of additives on both sorption and regeneration, powders between 50 and 80 mesh size were used. Powders were studied as opposed to formed beads to minimize the effect of shape and size and to obtain a better picture of the true activity of the materials as sorbents.

The apparatus used to evaluate effective SO_2 capacity and equilibrium capacity is shown in Figure 3. Essentially, this consists of carrier lines to provide a synthetic flue gas having the composition in mole %: 0.3% SO_2, 12.0% CO_2, 6.0% O_2, 5.6% H_2O and 75.9% N_2, a furnace for maintaining the sorbent at a relatively high temperature and a gas chromatograph for measuring SO_2 concentrations.

Gas of the composition indicated was passed through a reaction tube, containing a constant volume of the sorbent, enclosed in the furnace maintained at 600°F.

The effluent coming from the reaction tube was monitored for SO_2 concentration by gas chromatography. The break time (t_B) was defined as the time at which the effluent gas stream reached 5% of the SO_2 found in the feed gas stream. The break capacity was defined as the quantity of SO_2 sorbed per unit weight of the reactant during this time.

The apparatus used to evaluate the regeneration rate is shown in Figure 4.

FIXED-BED SORPTION TEST UNIT

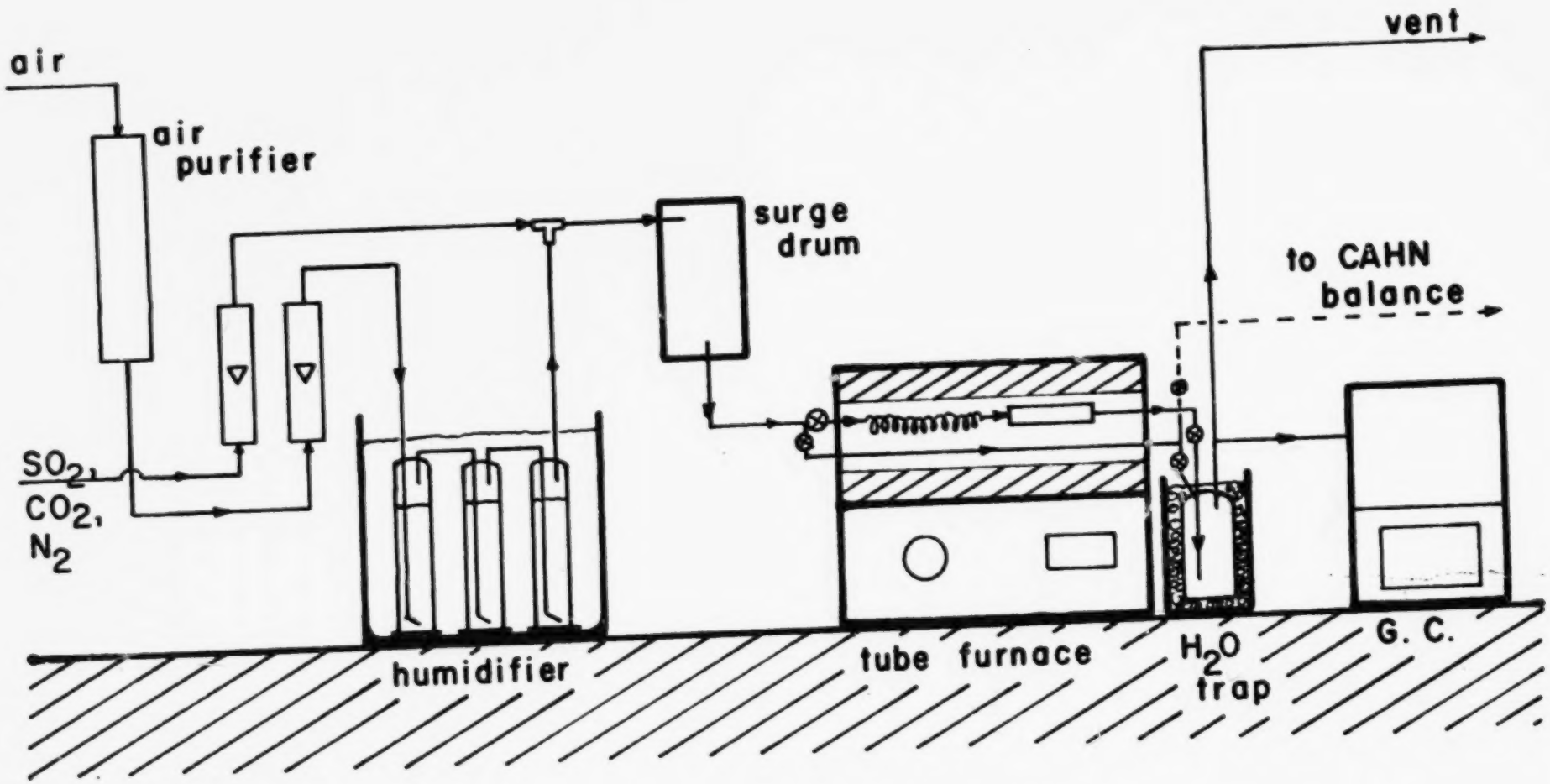


Figure 3: Schematic of Sorption Unit

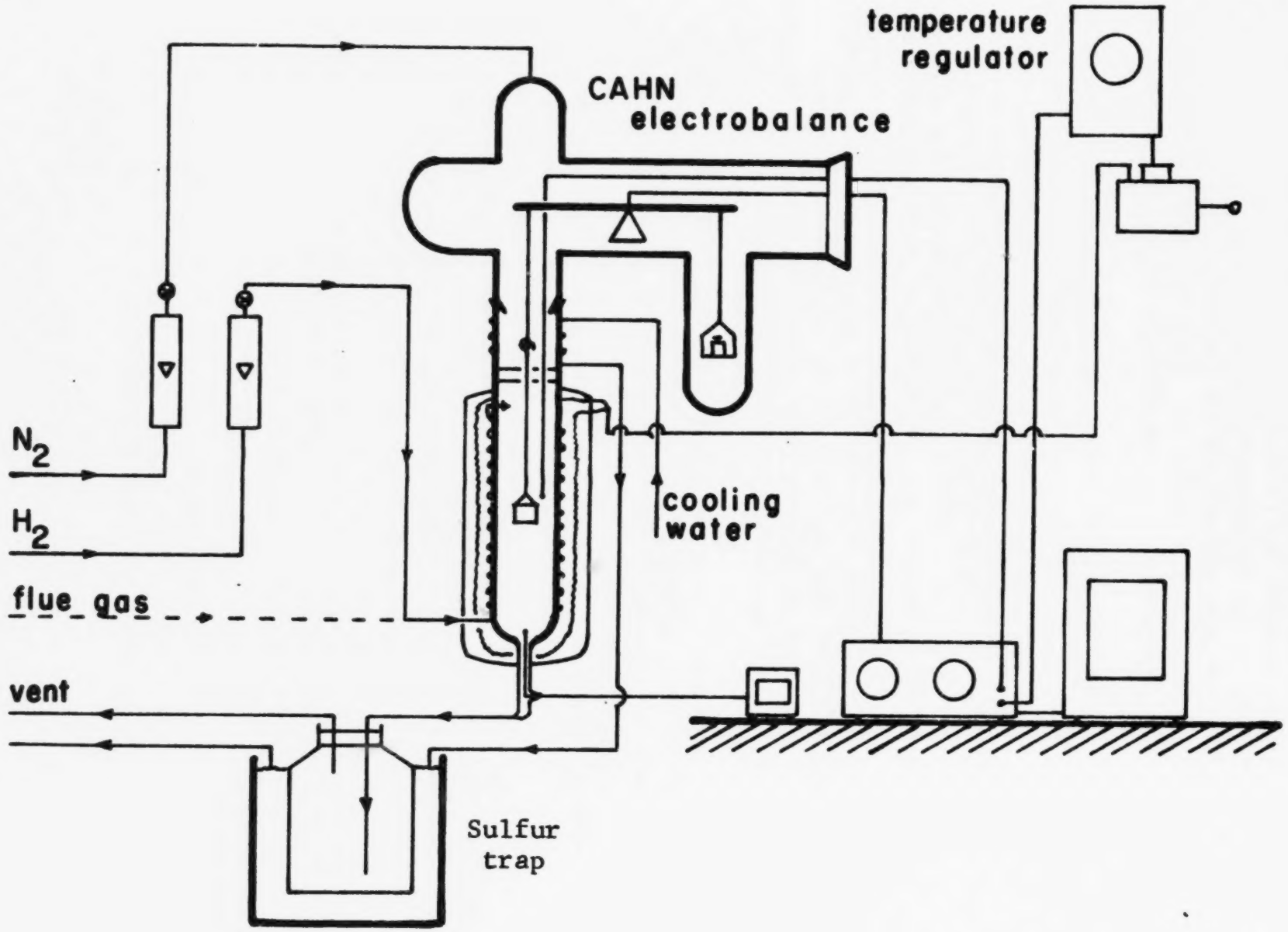


Figure 4: Schematic of Regeneration Unit

This system consisted of a Cahn electrobalance fitted with a thermostatically controlled furnace. It was so designed that hydrogen gas was preheated prior to flowing over the sample to be investigated. The weight loss of the sample vs. time at 1300°F was automatically recorded on a VOM Bausch & Lomb recorder.

Grace #1 was chosen as the initial standard. Table V shows this evaluation.

During the course of this work alkalized alumina was prepared under plant conditions using the modified Bureau of Mines procedure. After forming this product was designated Grace #2. The most significant difference found in this material was that the pore volume and surface areas were considerably improved. This material served as base for evaluation of all the additives studied, since it showed good sorption characteristics and contained essentially no Fe impurities.

This last was important since Fe was one of the additives to be studied. The most important single difference in the modified preparations was spray drying as opposed to a tray drying step during its preparation. Table VI compares these two products. The spray dried product is designated as 4928-48A.

It should be noted that the increase in pore volume and surface area resulted in an increase in break or effective capacity. The lowering of the % regeneration rate is attributed to the low iron content.

Using this spray dried material, a series of impregnations was made with various metal ions and in some cases combinations of ions. Iron impregnations were carried out using ferric-ammonium oxalate solutions.

Impregnations with Cu, Ni, Co and Cr were made with the acetate salts. In the case of vanadium, both sodium and ammonium vanadate were used.

TABLE V

EVALUATION OF GRACE #1 AFTER ACTIVATION AT 1100°F

Mercury Pore Vol. cc/g	= 0.69
N_2 Pore Vol. (cc/g)	= 0.51
B.E.T. Surface Area m^2/g	= 47.50

Chemical Analysis:

% Na_2O	- 35.40
% Al_2O_3	- 57.30
% CO_2	- 0.55
% SO_4	- 5.46
% Fe	- 0.36

% SO_2 sorbed at break capacity	= 17.70
% Regeneration	= 11.80

TABLE VI

EVALUATION OF GRACE #1 VS. SPRAY DRIED ALKALIZED ALUMINA

Sample	Hg.P.V. (cc/g)	S.A. (m^2/g)	Break Capacity Wt. %	% Regeneration Rate
Grace #1	0.69	47.5	17.7	11.8
4928-48A	0.92	69.0	24.4	6.9

The procedure for impregnation was to add solutions of the various salts to the sample of dawsonite and then evaporate the slurries to dryness. These products were then activated under H_2 at 1100°F for 5 hours and the performance determined. A total of 8 materials was studied. Table VII shows the evaluation results of the most promising materials.

These results show:

- Copper increases the break capacity, probably due to its oxidative activity.
- Iron and vanadium greatly improve the regeneration rate.
- Doubly promoted samples did not show a combining of the effects.
- Pt produces a good break-capacity and regeneration rate but is not economical.

Based in part on these results, a plant batch (6000 lbs.) was produced using the spray dried dawsonite and incorporating Fe in its preparation. This product after forming was sent to the Bureau of Mines for their evaluation. Our laboratory test of this sample, Grace #2, in powder form gave the following results:

Regeneration Rate	-	35.5 (%/min.)
Break-Capacity(Q_B)	-	24.0 %
Surface Area	-	74 m^2/g
Pore Volume	-	0.51 cc/g
Fe Content	-	0.6 %

2. Study of Regeneration Parameters

A study was made of the rate of regeneration as a function of reducing gas, temperature, and catalyst. Table VIII shows these relationships, and Figure 5 shows the plot of these relationships using H_2 regeneration. These results are summarized as follows:

TABLE VII

EVALUATION OF THE EFFECT OF ADDITIVES ON SORPTION AND REGENERATION

Sample No.	Additive	% Additive	Break Capacity (Q_B) Wt. %	% Regeneration Rate (%/min)
Grace #1	Fe	0.4	16.5	12.0
4928-48A	--	0.0	24.4	6.9
4607-48AF	Fe	1.0	23.8	35.9
4607-41	Cu	1.0	31.0	5.5
5245-1	Fe Cu	1.0 1.0	25.6	32.3
5119-17B	V from NH_4VO_3	1.0	19.6	55.2
5245-19	Pt	3.0	24.2	38.3

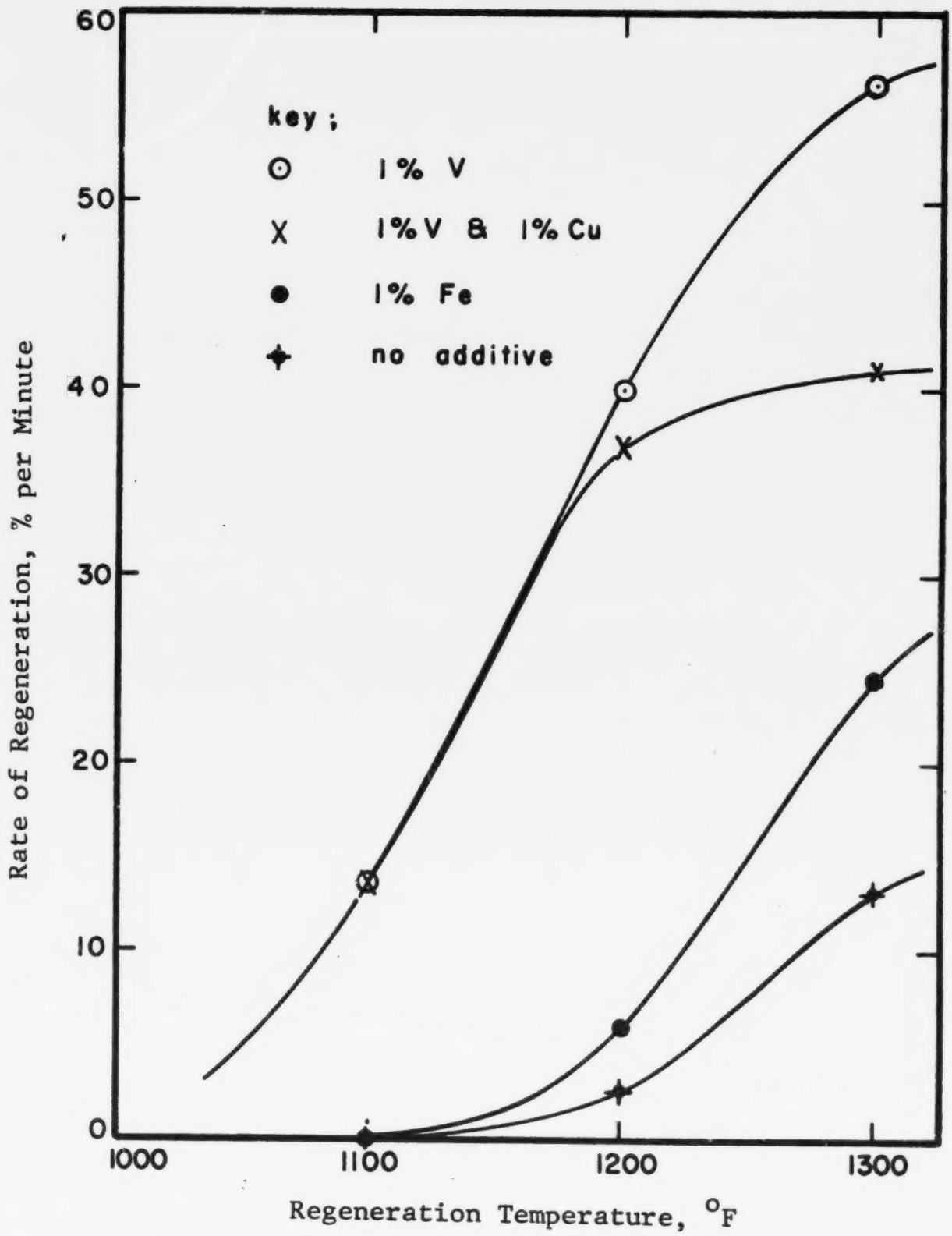


Figure : Effect of Promoters on Hydrogen Regeneration

TABLE VIII

SUMMARY OF REGENERATION STUDY

Sample		Grace #1	5213-34	5103-39	5213-5
Promoters		0.3% Fe	1% Fe	1% V	1% V and 1% Cu
Regeneration Gas	Temp. (^{o}F)	Rate of Regeneration (%/min)			
H_2	1100	N.M.*	N.M.	13.7	13.7
	1200	2.6	6.0	40.0	37.0
	1300	13.2	24.6	56.3	41.0
CH_4	1300	7.0	12.1	14.5	11.8
CH_4 with H_2O vapor	1300	4.7	12.2	17.0	11.7
Natural Gas ≠	1300	--	--	--	13.3
CO	1300	8.1		45.8	
C_2H_6	1100	--	--	N.M.	N.M.
	1200	--	--	19.7	26.3
	1300	--	--	26.3	58.8
C_3H_8	1100				18.0
	1200	--	9.0	27.7	44.3
	1300	23.8	--	--	50.4

* N.M. means not measurable (too slow)

≠ 95% CH_4 and 3% C_2H_6

- The regeneration temperature can be lowered 200°F (from 1300° to 1100°F) for hydrogen regeneration of vanadium or copper-vanadium promoted alkalized alumina.

- The doubly promoted (copper-vanadium) alkalized alumina is the best for use in the case of ethane or propane regeneration.

- Low cost natural gas was a workable regeneration gas.

The work described in this section was done prior to the discovery of the effect of NO_x on the sorption of SO_2. It will be shown in Section B that NO_x in the flue gas increases the rate of sorption but in the process significantly lowers the attrition resistance of the beads.

E. Endurance Testing of Formed Product

Useful sorbent life is a critical economic factor in the alkalized alumina process. It was necessary, therefore, to establish those parameters which affected the life of the sorbent with regard to useful capacity and resistance to attrition.

In order to accomplish this, the following objectives were set up:

- Development of a laboratory multicycle test to simulate plant scale aging behavior of various sorbents under standard conditions.

- Determination of the physical and chemical changes accompanying the aging process.

- Laboratory evaluation of the effect on sorbent life of a wide range of process conditions, and chemical variations in sorption or regeneration gas composition.

- Design and construction of two portable units to correlate data obtained in laboratory tests with normal catalyst aging using flue gas from coal burning furnaces.

1. Cyclic Aging Test Development

(a) Introduction

A standardized aging test was required to evaluate the life expectancy of activated alkalized alumina materials. First, however, it was necessary to determine the most important aging mechanism in order to establish the range of operating conditions in the equipment. Viewed against a background of experience in heterogeneous catalysis, a thermal or steam sintering mechanism under sorbent regeneration conditions seemed a strong possibility. In alumina and silica based catalysts sintering occurs at high temperatures and is accelerated by steam and alkali. It seemed probable that sodium aluminate, the active sorbent in activated alkalized alumina, would show similar reductions in surface area and growth in crystallite size under regeneration conditions. Such changes would be expected to reduce sorption efficiency. These effects could also be accentuated to provide an accelerated test by use of higher-than-normal regeneration temperatures coupled with steam or thermal pre-treatment.

(b) Results

Table IX shows the results of the steam and thermal aging evaluations. These data demonstrated that surface area is lowered by both parameters especially at the higher temperature. In both cases the pore volume was increased, as was the median pore diameter. It was also noted that steaming produced substantial crystallite growth.

(c) Discussion

The fact that artificial steam aging of the activated alkalized alumina produced extensive crystallite growth was considered in light of the sorption and regeneration process chemistry. In the initial activation step, dawsonite was converted to sodium aluminate.

TABLE IX

STEAM AND THERMAL AGING DATA

Treatment Conditions			Properties			
Temp., °F	Steam Volume in Air	Time (Hrs.)	S.A. (m^2/g)	P.V. (cc/g)	Median Pore Diam. Å	$NaAlO_2$ X-Ray Crystallite Size, Å
--	None		57	0.34	286	190(≠)
1380	100	8	25	0.52	886	910
1380	2.5	8	34	0.53	886	640
1200	28	4	22	0.43	886	-
1200	0	2	34	0.50	622	-
1020	100	4	26	0.62	1500	560
1020	100	4	37	0.59	622	360
1020	0	4	48	0.49	392	-
840	29	2	31	0.54	622	-
840	0	4	54	0.47	331	-

≠ These are values for fresh dawsonite

$$NaAl(CO_3)(OH)_2 \longrightarrow NaAlO_2 + H_2O + CO_2$$

The crystallite growth seen was that of sodium aluminate. In the sorption process all or part of the sodium aluminate was converted to sodium sulfate and aluminum oxide.

$$2NaAlO_2 + SO_2 + \tfrac{1}{2}O_2 \longrightarrow Na_2SO_4 + Al_2O_3$$

The degree of conversion depended on the sorbent loading reached in the actual process cycle.

Steam aging effects for mixtures of sodium sulfate and alumina were not determined but are presumed to be small relative to those for sodium aluminate. In any event, if regeneration was complete, these components reverted to sodium aluminate and underwent partial crystallite size reduction in so doing.

$$Na_2SO_4 + Al_2O_3 + 4H_2 \longrightarrow 2NaAlO_2 + H_2S + 3H_2O$$

The high temperature regeneration process also produced a severe environment in which steam sintering might occur. At low hydrogen space velocities (200 VHSV) water produced in the reaction was found to give steam concentrations of several percent. Predicting sintering rates in practice was difficult since at low sorbent loadings the steam concentration was lower but the quantity of unconverted sodium aluminate subject to attack was higher. At high loadings more steam was produced during regeneration, but more of the sodium aluminate was freshly formed from sodium sulfate and alumina.

It was predicted and then confirmed experimentally that high reduction space velocities would minimize steam aging effects at low sorbent loadings. Gas flows were established in the test procedures which insured steam concentration below 1% by volume would be maintained.

2. Multicycle Test

A multicycle test unit was designed to evaluate the aging characteristics of the sorbent in the laboratory under simulated plant conditions.

After considerable experimentation, sorption and regeneration cycles were established as shown in Table X. In twelve four-hour cycles the surface area was reduced to 31 m^2/g. Sorption efficiency declined from 4.5 to 3.0 wt. % sulfur sorbed in 90 minutes and appeared more dependent on declining pore volume than on surface area.

Using this procedure an extended multicycle aging run was carried out in order to prepare an extensively aged material. This run was made over 61 cycles. The decline in efficiency is shown in Figure 6.

The drop in effective capacity was attributed to loss of pore volume. This could have resulted from two factors.

- Plugging up of available pores by SO_4 accumulation on aging.
- Sintering of the $NaAlO_2$ during the high temperature regeneration (hydrothermal effects).

There was a leveling off of this decline at 2.6 wt. % sulfur pickup. This level of efficiency might be adequate in plant operations.

F. Chemistry of the Alkalized Alumina Process

Knowledge of the sorption and regeneration mechanism was necessary to determine the effect of physical structure and chemical composition on sorption efficiency. Several factors which would influence regeneration rates were also examined. The results are given below.

1. Activation Atmosphere

A study of activation atmosphere was made. This showed that there was little difference between activation in air and H_2. However, activation under N_2 showed much improved sorption. Mossbauer studies showed only the ferric state of iron to be present under all conditions and the reason for this effect remains unexplained.

TABLE X

STANDARD SORPTION - REGENERATION CYCLE*

Cycle Phase	Temp., °F	Time Lapse Minutes	% Gas Composition		Gas Flow @ S.T.P. cc/min.
Sorption	660	90	0.28	SO_2	2406
			4.71	H_2O	
			5.00	O_2	
			90.01	N_2	
Heat Up	--	24	100.00	N_2	520
High Temp. Stabilization	1170	12	100.00	N_2	1201
Regeneration	1170	75	9.99	H_2	1334
			90.01	N_2	
Cooling	--	21	100.00	N_2	1201
Low Temp. Stabilization	660	18	100.00	N_2	520

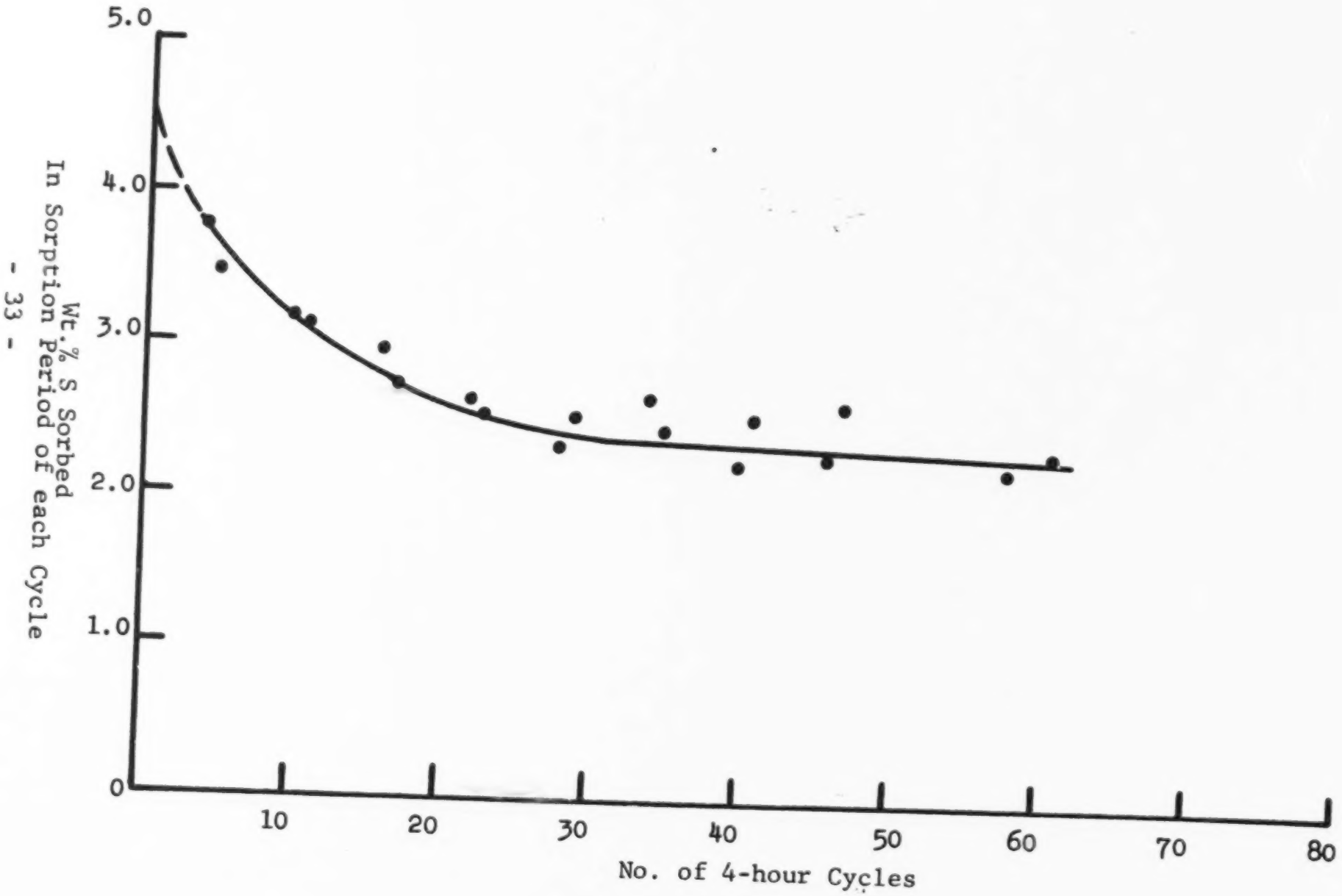
* Sample size of activated material is 32 cc.

ACTIVATION PROCEDURE*

Activation	1170	240	100.00	N_2	1201

* Initial volume of dawsonite is 40 cc.

Figure 6: Extended Aging - Grace #1



2. SO_2 Concentration and Space Velocity

For powder samples SO_2 sorption occurred at a rate dependent on both volume hourly space velocity (VHSV) of the gas and SO_2 concentration. That is, higher SO_2 loadings were obtained in a fixed time but the pickup efficiency dropped with higher SO_2 concentrations and higher space velocity.

3. Oxygen Level

It was shown that an oxygen concentration below 1% was too low to oxidize the SO_2 to SO_3, resulting in greatly decreased efficiency of SO_2 pickup. This also implies that the sorption as sulfite is less efficient than the sorption as sulfate at 660°F.

4. Temperature

A sorption run was carried out at 1200°F to examine the effect of higher temperatures on sorption. Higher temperatures were expected to more rapidly oxidize SO_2 to SO_3 when the SO_2 gas concentrations were in the range of 0.5%. Equilibrium calculations showed that 1000°F would have been better to use as at least 25% of the SO_2 remained unconverted at 1200°F. Data shown in Table XI[2] is for a run comprising two sorption and regeneration cycles on -50 +80 mesh Grace #1 alkalized alumina. At the conclusion of this run the sorbent had the properties shown in Table XII.

X-ray analysis of the sorbed phase showed that instead of the customary Na_2SO_4 formation, a sodium alum $Na_2Al(SO_4)_3$ was formed. Under the conditions of this experiment all x-ray detectable sodium alum was regenerable, although at a lower rate.

5. Effects of CO_2 on Sorption

Work at CERL indicated that at 450°F, CO_2 competed with SO_2 for the active sorption sites and that this competition could be avoided by increasing the temperature to 660°F. An alternative explanation is that the faster oxidative sorption mechanism is inoperative at 450°F. To distinguish between these possibilities, CO_2 was introduced into the

TABLE XI

SORPTION REGENERATION CHARACTERISTICS OF GRACE #1 ALKALIZED ALUMINA POWDER AT 1200°F OPERATING CONDITIONS

Cycle	Sorption VHSV	Breakthrough Time, Min.	Wt.% S Gain Break	Saturation Time, Min.	Wt.% Gain @ Saturation	Regeneration Time Min.
1	3970	380	16.6	554	20.6	185
2	3970	170	7.0	405	12.2	145

TABLE XII

MATERIAL CHARACTERISTICS BEFORE AND AFTER HIGH TEMPERATURE (1200°F) OPERATION

	Before	After
Pore volume, cc/gm	.54	.36
Surface Area, m^2/gm	64	15
Average Pore Diameter, Å	331	886
Crystallite Size ($NaAlO_2$), Å	~200	275

sorption gas stream at various oxygen concentrations. The results of these tests appear in Table XIII.

At low oxygen levels (ca. 0.5% O_2) where both SO_2 conversion to SO_3 and sorption were inefficient, the addition of 10% CO_2 apparently improved the sorption rate. However, where sufficient oxygen pressure was present for stoichiometric conversion of SO_2 to SO_3, CO_2 hindered the sorption rate and reduced the breakthrough capacity at 660°F. This also occurred with oxygen far exceeding the stoichiometric requirement. It would appear, then, that even higher temperatures than 660°F might be needed to fully overcome the CO_2 retarding effect at the high CO_2 concentrations expected in the flue gas stream of power plants.

The presence of CO_2 also indicates a somewhat higher sorbent attrition rate. The reasons for this are presently unknown.

6. Effect of NO_x on Sorption

It was shown that NO_x in the flue gas substantially increased the sorption rate of sulfur on formed sorbents. A catalytic reaction with SO_2 to form SO_3 was suspected.

In addition to this beneficial effect, it was also discovered that NO_x produced a very serious loss of attrition resistance. In the laboratory, using a flue gas composition free of NO_x, after 1 cycle of sorption and regeneration,. a second degree severity (see appendix for test details) attrition loss of 7 to 10% maximum was obtained on Grace #2.

In one cycle at the Crane station of the Baltimore Gas and Electric Co. (using the same Grace #2) the attrition loss was more than 35%.

As a result, a series of laboratory tests was performed to find which flue gas component was responsible for the unusually high attrition loss. Table XIV shows the gas compositions used and the results obtained. This data clearly showed that NO even in low concentrations severely affected attrition resistance.

TABLE XIII

EFFECTS OF CO_2 ON SORPTION @ 660°F

% Oxygen Concentration	% CO_2 Concentration	VHSV	Breakthrough Time, Min.	Wt.% S Gain @ Break	Wt.% S. Gain @ 150 Min.
0.5	0	4000	40	2.0	5.0
0.5	10	4000	75	3.6	7.2
1.0	0	4000	81	4.0	6.7
1.0	10	4000	50	2.2	5.2
5.0	10	4000	48	2.2	6.6

TABLE XIV

FLUE GAS COMPOSITION VS. ATTRITION RESISTANCE

Sample #: Grace #2						
Run #	1	2	3	4	5	6
Gas Composition						
% SO_2	0.28	0.28	0.28	0.28	0.28	0.28
% H_2O	4.71	5.00	5.00	5.00	5.00	5.00
% O_2	5.00	5.00	5.00	5.00	5.00	5.00
% N_2	90.01	74.72	74.62	74.67	74.71	74.11
% CO_2	-	15.00	15.00	15.00	15.00	15.00
% HCl	-	-	0.10	-	-	-
% NO	-	-	-	0.05	0.01	0.05
Gas Flow, cc/min.	2640	2640	2640	2640	2640	2640
Temperature, ^{o}F						
Sorption	660	660	660	660	660	660
Regeneration	1209	1209	1209	1209	1209	1209
Number of Cycles	1	1	1	1	1	1
Attrition Loss, %, 2nd^{o}	~6.0	11.4	13.4	50.8	52.4	79.2
Time of Exposure to Sorption Gases, Min.	90	90	90	62	60	90

7. Effect of Poisons

Chlorine and arsenic were introduced into the synthetic flue gas stream in concentrations of 0.19 and 1.0% respectively. Neither adversely affected sorption. However, it was found that arsenic prolonged the normal regeneration time. It was assumed that the arsenic reacted with the iron to form either FeAs or $FeAs_2$ and thus poisoned the catalyst required for rapid hydrogen activation.

8. Effect of CO_2 on Regeneration

Grace #1 alkalized alumina powder loaded to about 1/3 of its capacity with SO_2 was regenerated with 0, 5 and 10% CO_2 in the 80% hydrogen gas stream. The effect of CO_2 is shown in Table XV. It is apparent that 10% CO_2, more than halved the normal regeneration times. This was due to the formation not only of H_2S but also COS in the reductive process. No carbon formation was observed. On the basis of the reduction in regeneration time, it is recommended that carbon dioxide with hydrogen or some other reducing gas may be used during the regeneration step to permit lower regeneration temperatures and minimize the aging rate normally found.

G. Portable Aging Units

Two portable aging units were designed and built for the purpose of examining sorbents under actual plant conditions. One of the units was placed in operation at the Dickerson, Maryland, generating stations of the Potomac Electric Power Company. This station is coal fired using coal which contained up to 2% by weight sulfur. The second unit was located at the Crane station of the Baltimore Gas and Electric Company.

Extensive use of these units resulted in the discovery of two important sorption and regeneration phenomena. These were the detrimental effect of NO_x on bead attrition properties and the accumulation of free sodium chloride presumably formed during regeneration from excess soda in the bead reacting with chlorine from the stack gases. Further, an estimate of useful sorbent life of improved products was obtained from these studies.

TABLE XV

EFFECT OF CO_2 ON REGENERATION*

		Run No.		
		28	23	24
Regeneration Gas Composition	$\%H_2$	80	80	80
	$\%CO_2$	0	5	10
	$\%N_2$	20	15	10
Wt. % Sorbed		7.85	8.12	7.60
Pore Volume, cc/g		0.42	0.48	NA
Surface Area, m^2/gm		20	19	29
Avg. Pore Diameter, Å		622	622	NA
Time (Min.) to 0.2% H_2S in Exit Gas Stream		140	150	70

* Regeneration Gas, VHSV = 276;
Regeneration Temperature 1200°F

NA - Not Available

SECTION B

SCREENING NEW SORBENTS FOR IMPROVED ATTRITION RESISTANCE

I-B. Introduction

Two factors were principally responsible for the severe reduction in resistance to attrition of unbound formed alkalized alumina.

- Sodium aluminate crystallite growth during regeneration.
- Accelerated sorption at and near the surface due to the presence of NO_x in the flue gas.

We had previously shown that growth in $NaAlO_2$ crystallite size occurred at elevated temperatures and relatively low steam concentrations (3%). When sorption of SO_2 was oxidation rate limited (i.e. in the absence of NO_x) sulfate buildup appeared uniformly throughout the bead. Regeneration by sulfate reduction in H_2 produced H_2S and steam evenly throughout the particle, thus accelerating uniform crystallite growth. It was postulated that the crystallite growth destroyed the cohesive quality of the original particle.

The influence of crystallite size attrition resistance under these circumstances is shown in Figure 1. Laboratory single cycle (sorption/regeneration) experiments on Grace #2 without NO_x showed a maximum attrition loss of 10%. Attrition loss increased to 100% when NO_x was introduced to the synthetic flue gas stream.

In the presence of NO_x, SO_2 sorption became diffusion rate limited, thus concentrating the sulfate buildup as a shell beginning at the beads' outer surface. Grace #2 material examined after exposure to flue gas containing NO_x exhibited a severely cracked shell which led to the 100% attrition loss observed.

On the basis of this physical picture, the investigation of binder systems was begun. Binder systems were investigated which would not be severely attacked by SO_2 and would create sufficiently strong interparticle bonds which could resist rupture by the rearrangement and physical growth of the sodium aluminate crystals. Dawsonite sorbents were prepared using many materials as binders and evaluated by test procedures adopted during the investigation.

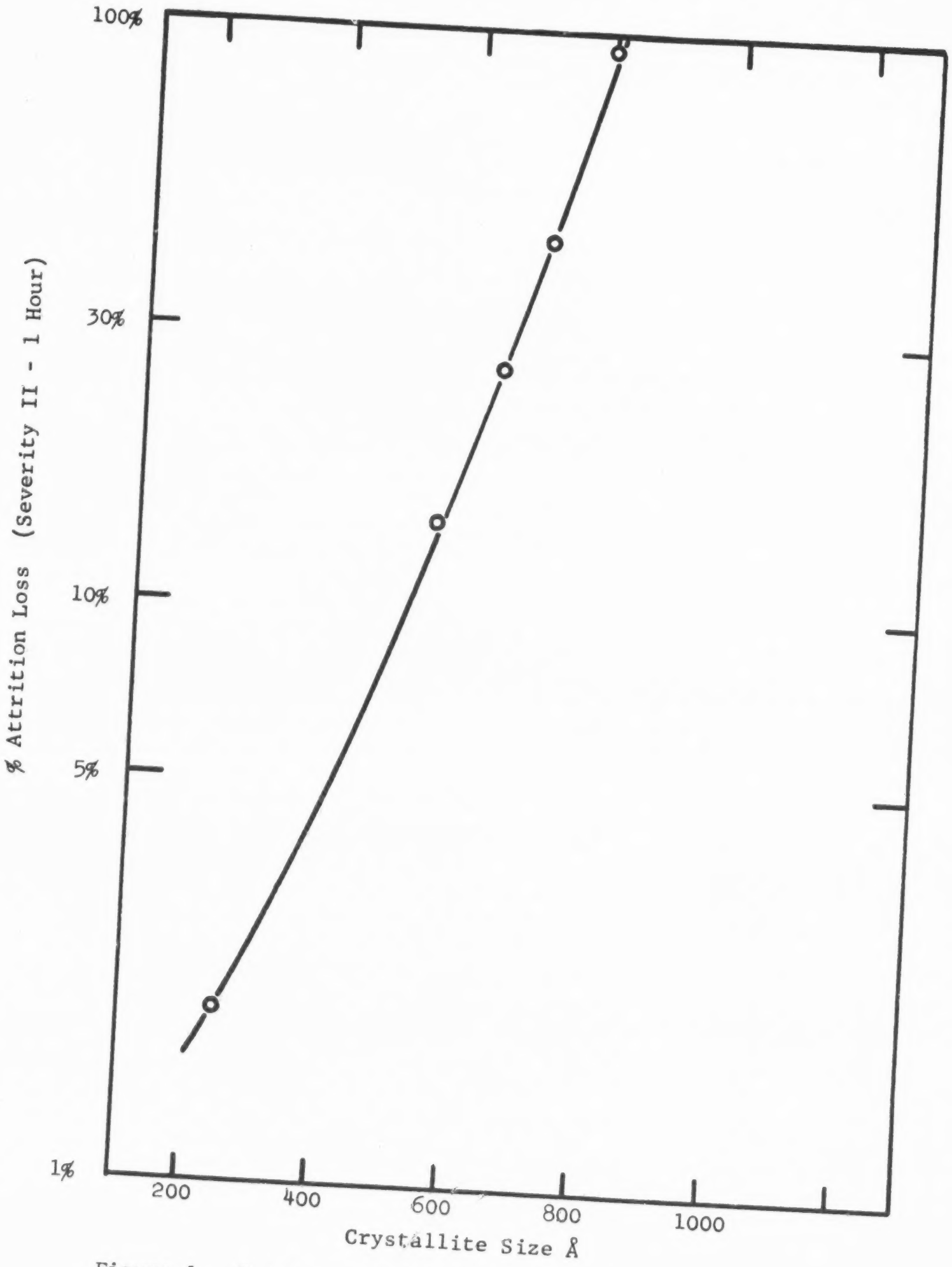


Figure 1: % Loss vs. Crystallite Size for Grace #2 Alkalized Alumina in Laboratory Tests (No NO_x in Flue Gas)

A second approach to the attrition problem was to impregnate with sodium aluminate carriers of good attrition resistance and stability to an acid environment.

In addition to these approaches, other process variables which might affect attrition were also studied.

The following materials were investigated as potential binder materials:

- Kaolin
- Meta-kaolin (calcined kaolin)
- Avery Clay
- Bauxite
- Bentonite
- Asbestos
- Jamaica Red Mud
- Silica (gel, sol)
- Alumina (gel, sol)
- Cement (Portland Type I, Type V)
- $CaSO_4$
- $CaCO_3$
- Meta-kaolin + NaOH
- Kaolin + NaOH
- Kaolin + Na_2SiO_3
- Avery Clay + Na_2SiO_3

The process variables studied were:

- Sorption temperature
- Regeneration conditions
- Activation conditions

II-B. Details

A. Methods of Sample Preparation

1. Binder Incorporation and Beading Technique

In all preparations using a binder, the alkalized alumina was prepared essentially by the Bienstock procedure. The material was spray dried and iron oxide added as the regeneration catalyst.

The general laboratory procedure was to premix, as dry powder, the binder, iron oxide and alkalized alumina for a period of one-half hour in a "V" blender. 75% of the premixed powder was then placed in a Day Company pony mixer, and mixed, with the slow addition of water, until cohesive beads took shape. The remaining 25% of starting powder was used to dry back the beads formed and to prevent excessive agglomeration.

In those cases where sodium silicate was used, it was first diluted to supply about half of the water required for the beading operation. This silicate solution was added to 75% of the original powder. Beading then proceeded according to the general method, using the remainder of the water as necessary.

2. Impregnation

Two slightly different methods were used as explained in (a) and (f).

(a) A saturated solution of sodium aluminate was prepared at room temperature (alternate procedure: a weaker solution (40% sodium aluminate) was prepared at room temperature).

(b) A quantity of alumina beads previously activated at 600°F for 2 hours was weighed and placed in a 500 ml round bottom flask.

(c) Using dropwise addition, sodium solution was added to incipient wetness with thorough shaking.

(d) The wet beads were heated at 600°F for 2 hours.

(e) The following data were obtained:

Na_2O Analysis

S.A. (m^2/g)

P.V. (cc/g)

X-ray Diffraction Pattern

(f) Steps (a) through (e) were repeated until Na_2O analysis showed no further change.

(g) A solution of ferric ammonium oxalate was added to give a 1% iron content based on the total weight of dry beads.

(h) The liquid from beads was evaporated to dryness.

The following supports were investigated:

- Kaiser γalumina
- Pechiney γalumina
- Norton alundum
- Norton silicon carbide
- U.O.P. γalumina

B| Evaluation for Sorption Efficiency and Attrition Resistance

In order to properly evaluate the new materials, it was necessary to develop rapid but discriminating screening tests. The following methods were adopted.

- A severe single cycle test for preliminary screening.
- A multicycle aging test to simulate plant scale aging behavior.
- A final check was then made using plant-site field testing units.
- The effect of process conditions on activation, sorption, regeneration and attrition were determined.

1. Single Cycle Screening Test

Since it was shown that NO_x increased the efficiency of sorption, but adversely affected attrition resistance, a single cycle test was developed in which 0.05% NO was present in the synthetic flue gas. The concentration of SO_2 was 0.84% (considerably above the normally present plant operating conditions) to accelerate the physical degradation of the sorbents.

2. Multicycle Aging Test

The incorporation of NO and CO_2 into the previously established standard laboratory sorption flue gas gave multicycle test data comparable to field test data for sorption efficiency and attrition resistance. Table I shows a comparison of attrition results from 7 cycle laboratory tests with those from multicycle field tests for two different sorbents.

3. Process Variables

Several process variables were studied to determine their effect on sorption, regeneration and attrition.

(a) Sorption Temperature

Useful SO_2 sorption rates were found to exist in a temperature range of 260°F to 1000°F; however, the sorption mechanism was dependent upon the temperature employed. From 260°F to 800°F, SO_2 was probably oxidized by NO_2 to SO_3 in the gas phase with the sorption rate (as SO_3) being diffusion controlled.

TABLE I

COMPARISON OF RESULTS FROM LABORATORY AND FIELD UNITS

Sample	Heat Treatment at 1600°F(hrs)	Laboratory Unit # Cycles	Field Unit # Cycles	% Attrition Loss Thru 16 Mesh
Grace #2	0	7	-	18
Grace #2	0	-	27	78
RL-175 23% Kaolin 2% Na_2SiO_3 75% Dawsonite 1.8% Fe	0	7	-	30
"	0	-	46	30

This led to surface sorption and "eggshell" cracking. From 800°F to 1000°F, NO_2 is increasingly dissociated to NO, thus reducing the amount available to oxidize SO_2. Consequently at the higher temperatures, Sorption of SO_2 became oxidation rate controlled and a substantial reduction in attrition loss of the beaded alkalized alumina was seen. Unfortunately the sodium aluminate forms a less easily regenerable compound at 1000°F. Table II shows the results obtained.

(b) Regeneration

A two-step regeneration mechanism was evaluated to determine feasibility. Carbon monoxide was shown to be an effective reducing agent at 1200°F for the reaction:

$$Na_2SO_4 + 4CO \longrightarrow Na_2S + 4CO_2$$

Regeneration was then most effectively completed at 450°F with a 3/1 gas stream of CO_2 and H_2O vapor. The two-step method was found to be more effective in total sulfur removal than hydrogen alone at 1200°F. The added mechanical complications may well restrict the utility of this procedure.

(c) Activation

Activation conditions were evaluated for kaolin-bound dawsonite, the precursor to the active $NaAlO_2$ sorbent. High air sweep rates through the bed were required to minimize hydrothermal aging accompanying the dehydration and/or the decomposition of $Al(OH)_3$, dawsonite and hydrated binder material (kaolin). The most effective use of clay as a binding material required a further calcination step to initiate reactions between sodium aluminate and the silica in the clay to form a ceramic phase (carnegieite). Table III shows the effect of activation conditions and Table IV the effect of heat treatment and binder type on attrition loss.

Kaolin bound dawsonite produced a marginal improvement over Grace #2. However, by heat treating the

TABLE II

EFFECT OF SORPTION TEMPERATURE ON ATTRITION RESISTANCE OF GRACE #2

Sorption Temp. ^{o}F	% NO in Flue Gas	Attrition Loss,%
260	0.05	100
600	0.10	100
1000*	0.05	1-2

* Material resulting from this sorption was $NaAlSO_4$ not $NaSO_4$ as normally found at $660^{o}F$ sorption temperature. This material was difficult to regenerate.

TABLE III

EFFECT OF ACTIVATION CONDITION ON ATTRITION PRIOR TO SORPTION

Sample	Activation Condition	% Loss Thru 16 Mesh
RC-174 25% Kaolin 73% Dawsonite	1200°F/4 hrs. Air Sweep	8
"	800°F/2 hrs. followed by 1020°F/ .5 hr. 1120°F/ .5 hr. 1200°F/ 3 hrs. all with static air	18
"	1200°F/ 4 hrs. static air	98

TABLE IV

EVALUATION OF KAOLIN BINDERS AND EFFECT OF HEAT TREATMENT ON ATTRITION

Sample No.	Binder	Heat Treatment @1600°F (hrs.)	% S Sorbed	% Attrition Loss On 16 Mesh	% Attrition Loss On 60 Mesh
RC-174A	25% Kaolin	0.0	7.82	88.2	80.5
"	"	1.0	8.49	37.6	33.0
"	"	4.0	8.57	66.0	59.0
RL-175	23% Kaolin 2% Sodium Silicate	4.0	6.60	10.7	9.4
Grace #2	0.0	4.0	12.60	96.1	71.8

bound samples at 1600°F, a substantial improvement was obtained. The reason for this is believed to be the formation, during the heat treatment, of carnegieite ($Na_2O \cdot Al_2O_3 \cdot 2SiO_2$).

The kaolin and sodium silicate bound sample showed considerably more improvement. The reason for this is not known but may be due to enhanced binding caused by additional formation of carnegieite. This might result from greater availability of soda and silicate from sodium silicate.

III-B. Conclusions and Recommendations

The most promising of the many materials investigated as binders are shown in Table V and are compared to binder-free alkalized alumina (Grace #2).

Table VI shows the most promising of the six sodium aluminate impregnated carrier systems investigated. As a result of the screening work the composition and process shown in Table VII were recommended for further development.

Although small pilot plant scale production of this material gave good results (Sample No. RL-175, Table V), a large plant scale preparation gave attrition approaching 100%. Two reasons were advanced for the lack of attrition resistance observed in the plant run.

- The formation of appreciable β-alumina trihydrate in the large scale preparation of dawsonite.
- Scale-up difficulties and lack of control in the extruding and rolling steps during forming leading to poorly compacted beads.

The laboratory and pilot plant work which led to a solution of this problem is described in Section C.

TABLE V

EVALUATION OF ALKALIZED ALUMINA BINDERS

Sample No.	Binder	% Binder	Heat Treatment @ 1600°F (Hrs.)	%S Sorbed	% Attrtition Loss Through 16 Mesh U.S. After Severe Cycle of Sorption & Regeneration
RC-174	Kaolin	25.0	1.0	8.49	37.6
RL-175	Kaolin Na_2SiO_3	23.0 2.0	4.0	6.61	10.7
5759-16	Metakaolin	25.0	1.0	7.50	18.0
5759-C	Kaolin Na_2CO_3	16.8 8.1	4.0	5.38	22.8
Grace #2	None	-	4.0	12.61	96.1

TABLE VI

EVALUATION OF CARRIERS IMPREGNATED WITH SODIUM ALUMINATE

Sample No.	Alumina Source	% S Sorbed	% Attrition Loss Thru 16 Mesh U.S. After Severe 1 Cycle of Sorption and Regeneration
5613-14	Kaiser γ-Alumina	6.0	15.1
5532-36B	Pechiney γ-Alumina	5.0	18.6

TABLE VII

COMPOSITION AND PROCESS RECOMMENDED
FOR FURTHER DEVELOPMENT

Sorbent Composition

75% Dawsonite

23% Kaolin

2% Sodium Silicate

1% Fe based on total dawsonite

Conditioning

Activation - 1200°F/4 hours with air sweep

Heat Treatment- 1600°F/4 hours static air

SECTION C

LABORATORY AND PILOT PLANT PRODUCTION OF ATTRITION RESISTANT SORBENTS

I-C. Introduction

As a result of work carried out in Section B, it was shown that several binder systems had good sorption and attrition resistance characteristics. The work reported in this section shows reproducibility in the preparation of these products as measured by their sorption and attrition values.

In addition, an improved technique was developed for producing well formed product. The sophisticated five module automated field test unit was completed and checked for proper operation. (See Appendix B).

II-C. Details

A. Laboratory Preparations

Table I gives a summary of the kaolin bound sorbents which earlier gave good attrition resistance. The preparations of these products were repeated as described below:

1. Precipitation of Dawsonite in the Presence of Binders

These preparations in general followed the Bienstock method.

(a) To 4000 ml of H_2O was added 764 grams of Na_2CO_3 (anhydrous) and the solution was heated to 90°C.

(b) A second solution was prepared by adding 1332 grams of $Al_2(SO_4)_3 \cdot 18H_2O$ to 2000 ml of H_2O and heating to 90°C.

(c) To the solution of Na_2CO_3 was added 345 grams of kaolin. This slurry was mixed well for 10 minutes.

(d) The solution of aluminum sulfate was then added slowly to the sodium carbonate-kaolin slurry.

(e) This reaction mixture was then allowed to stand with stirring for two (2) hours at 90°C.

(f) After this two hour period 14.7 grams of Fe_2O_3 were added and mixed for 10 minutes.

TABLE I

SUMMARY OF RESULTS ON BOUND AND FORMED ALKALIZED ALUMINA

Sample No.	Binder	% Binder	Heat Treatment 1600°F(hrs)	%S Sorbed	% Attrition Loss Thru 16 Mesh U.S.
RC-174	Kaolin	25.0	1	8.5	37.6
RC-174	Kaolin	25.0	4	8.7	66.0
RL-175	Kaolin	23.0			
	Ma_2SiO_3	2.0	4	6.6	10.7
5759-9B	Alumina	14.5			
	Na_2SO_4	10.5	0.5	5.3	36.4
5759-2C	Kaolin (in-situ prep)	25.0	4	4.5	19.8
5759-6C	Kaolin	16.8			
	Na_2CO_3	8.1	4	5.4	22.8
5759-16	Meta-kaolin	25.0	1	7.5	18.0
Grace #2		-	4	12.6	96.1

(g) The resulting slurry was allowed to cool and stand at room temperature for 16 hours.

(h) The slurry was then filtered and washed three times with 2000 ml portions of a 3% Na_2CO_3 solution.

(i) The filter cake was then allowed to air dry to a consistency suitable for beading in a Day Co. pony mixer.

(j) During the beading operation, the beads were surface dried by the addition of 400 grams of a powder having the same composition.

(k) The resulting beaded product was then allowed to dry overnight in a 110°C oven and then sieved on U.S. 10 - 12 mesh screen.

(l) The product at this stage was examined for surface area, pore volume, D.T.A., x-ray, and soda content.

The mole ratio of Na_2CO_3 to $Al_2(SO_4)_3$ used here was 3.6/1 and the theoretical yield of dawsonite was 1036 grams. The quantities of reactants used to prepare dawsonite were kept constant during the several preparations and only the quantity of binder was changed.

2. Meta-Kaolin Preparation

(a) To 1200 grams of dawsonite was added 300 grams of meta-kaolin and 17 grams of Fe_2O_3 to give 1% Fe based on total dawsonite used.

(b) This mixture was blended for one (1) hour in a "V" blender.

(c) 3/4 of the blended powder was placed in the pony mixer and beaded by spraying approximately 1500 cc of water into the mix.

(d) The remaining 1/4 of the dry powder was used to dry back the wet beads.

(e) This mix was placed in an oven at 110°C for 16 hours and then sieved through 8 - 16 U.S. standard mesh screen.

(f) The product was examined as in (e) above.

Tables II and III, attached, list each preparation with its physical properties after drying.

In addition to the preparations tabulated, a repeat evaluation was made of an impregnated alumina. As previously reported, an alumina produced by the Davison Chemical Division had been used to prepare an impregnated sorbent. The attrition of this material (Sample No. 6019-8) was found to be 89% in preliminary screening.

The severe single cycle sorption and regeneration test was repeated. The attrition was 100%, so no further consideration was given to this sorbent.

Table IV gives the evaluation of all samples prepared on laboratory scale.

B| Pilot Plant Preparations

Laboratory and small scale pilot plant preparations of a bound-dawsonite product (23% kaolin, 2% sodium silicate, 75% dawsonite) demonstrated good resistance to attrition. However, this same formulation failed to demonstrate a similar attrition resistance when produced at plant scale.

Two possible reasons were advanced to account for this difficulty.

- The formation of appreciable quantities of crystalline β-alumina trihydrate in the large plant preparation of dawsonite.
- Scale up difficulties in the forming method which produced poorly compacted beads.

As a result of laboratory work reported in this section, the forming method was implicated while the presence of β-alumina trihydrate was demonstrated to have little influence on the observed reduction in attrition resistance. Consequently, work proceeded on the development of a new forming method.

A successful forming method was developed using a machine known as a Marumerizer. This equipment operated by rotating

TABLE II

PHYSICAL EVALUATION OF INSITU BINDER PREPARATION

Sample No.	Dawsonite Crystallite Size	Binder	% Binder	S.A. $m^2/g.$	P.V. cc/g.	X-Ray Identification	D.T.A. Temp. °C of Endotherm	$\%Na_2O$
6019-10-1	115Å	Kaolin	25	79	0.27	Dawsonite & Kaolinite B-trihydrate	130°C(M) 300°C(M) 350°C(L) 430°C(S)	14.3
6019-10-2±		Kaolin	25					
6019-10-3	130Å	Kaolin	20	89	0.32	Dawsonite & Kaolinite B-trihydrate	140°C(M) 295°C(M) 355°C(L)	14.2
6019-12-4		Kaolin	15	--	--	"		
6019-12-5	125Å	Kaolin	25	--	--	"	-	13.4
6019-12-6	115Å	Meta-Kaolin	25	--	--	Dawsonite B-trihydrat3	-	14.33
6019-12-7	130Å	Kaolin	25	--	--	Dawsonite	-	13.40

± In this preparation an attempt was made to extrude the product. However, we were not successful in producting extrusions of the proper size

S = Small, M = Medium, L = Large

TABLE III

PHYSICAL EVALUATION OF META-KAOLIN BINDER DRY BLENDED

Sample No.	Sample Crystallite Size Å	Binder	% Binder	S.A. m^2/g	P.V. cc/g	X-Ray Identification	D.T.A. Temp. °C of Endotherm	% Na_2O
6019-11-1	130	Meta-Kaolin	25	61	.21	Dawsonite & B-trihydrate	140 (S) 290 (M) 360 (L)	16.1
6019-11-2	170	Meta-Kaolin	25	67	.23	Dawsonite & B-trihydrate	140 (S) 290 (M) 360 (L)	14.6
6019-11-3	123	Meta-Kaolin	25	99	.18	Dawsonite & B-trihydrate	130 (M) 290 (M) 360 (L)	12.9
6019-11-4	130	Kaolin	25	49	.14	Dawsonite & Kaolinite B-trihydrate	130 (S) 290 (M) 360 (L) 430 (S)	14.6
6019-13-1	123	Meta-Kaolin Na Silicate	23 2	51	.17	Dawsonite & Kaolinite B-trihydrate	140 (S) 300 (M) 355 (L) 430 (S)	14.7

S = Small, M = Medium, L = Large

TABLE IV

SORPTION AND ATTRITION EVALUATION OF VARIOUS SAMPLES

Sample No.(2)	Binder	% Binder	Heat Treatment @1600°F(hrs)	S.A. (m^2/g)	P.V. (cc/g)	% S Sorbed	% Attrition Loss on 16 Mesh-U.S.	Remarks
5808-74A (6019-11-4)	Kaolin	25	1	-	-	-	19.4	Standard Powder Blend
5808-72B (6019-12-4)	Kaolin	15	4	-	-	7.8	16.3	"
5808-63A (6019-10-1)	Kaolin	25	1	21	.38	3.78	41.7	Insitu-Prep.
5808-63B (6019-10-1)	Kaolin	25	4	-	.43	-	41.8	"
5808-62A(1) (6019-11-1)	Meta-Kaolin	25	1	25	.38	7.26	6.8	Dry Powder Blend
5808-62B(1) (6019-11-1)	Meta-Kaolin	25	4	19	.45	6.19	15.6	Dry Powder Blend
5808-70A(1) (6019-11-3)	Meta-Kaolin	25	1	-	-	7.39	13.7	"
5808-70B(1) (6019-11-3)	Meta-Kaolin	25	4	-	-	6.92	15.6	"
5808-73A (6019-13-D1)	Kaolin Na_2CO_3	16.8 8.1	1	-	-	7.99	26.9	"
5808-73B (6019-13-D1)	Kaolin Na_2CO_3	16.8 8.1	4	-	-	8.6	13.75	"

(1) All samples were activated at 1200°F for four hours prior to heat except those noted which were activated at 800°F for four hours.

(2) All numbers in brackets refer to the samples after preparation and drying. All numbers without brackets refer to the same samples after heat treatment.

a specially machined grid plate in a stationary cylinder. The centrifugal force of the grid plate threw the feed material, in this case extrudates, against the outer stationary wall where friction created a rolling action moving the material in an outward spiral. As rolling progressed the segmented extrudates were shaped into compacted spherical beads. At constant operating conditions the time required for sphere formation depended upon the properties of the feed material. However, the Marumerizer could be adjusted to vary the time required. The formed spheres were then discharged through an opening in the side of the stationary cylinder.

Three separate preparations of the bound system (23% kaolin, 2% sodium silicate, 75% dawsonite) varying only in water content were formed using this equipment. These samples were evaluated using the severe single cycle test with the best one field tested for 46 cycles at the Crane station of the Baltimore Gas and Electric Co. Table V shows the results obtained.

III-C. Conclusions and Recommendations

- It was at first thought that the presence of β-alumina trihydrate in the dawsonite prior to forming was associated with poor attrition resistance. We have since learned that a very good product can be obtained even with β-alumina trihydrate present. The problem of attrition resistance lay primarily in the forming technique. Good samples were prepared in small batches using a Day Co. pony mixer and in larger pilot plant batches using a Marumerizer.

- All of the systems reported showed considerable improvement over binder-free dawsonite.

- Precipitating the dawsonite in the presence of kaolin did not produce superior products.

- Heat treatment at 1600°F was necessary to produce a good attrition-resistant product.

- Meta-kaolin bound dawsonite produced a very good attrition resistant product. The activation temperature required prior to the heat treatment was only 800°F as opposed to the 1200°F required for kaolin bound samples.

TABLE V

EVALUATION OF BEADS MADE USING MARUMERIZER

Sample No.	Binder	Field Tested 46 Cycle	Tested Using Severe Single Cycle	% S Sorbed	Attrition Thru 16 Mesh U.S.
5808-55B Batch #1	23% Kaolin 2% Na_2SiO_3	No	Yes	6.42	9.4
5808-56B Batch #2	"	No	Yes	6.54	37.5
5808-57B Batch #3	"	No	Yes	5.59	20.0
5808-55B Batch #1	"	Yes	-	-	4.6

- The Marumerizer should be used to prepare the formed product.

The most promising materials prepared were:

(a) 25% meta-kaolin, 75% dawsonite

(b) 23% kaolin, 2% sodium silicate, 75% dawsonite

There appeared to be little to choose between these two preparations. However, since (b) was prepared on a pilot plant scale and was also evaluated in a 46 cycle field test, it is recommended for any future larger scale production.

A P P E N D I X

A. Modified Air Jet Attrition Test

B. Sophisticated 5 Module Field Test Unit

C. Organization Chart

APPENDIX A

Modified Air Jet Attrition Test

Because of the need for outstanding attrition characteristics of a sorbent, a new attrition test was developed for testing alkalized alumina beads. The test is based upon one developed to determine attrition of catalysts used in refineries. The petroleum industry finds good correlation between the test and attrition in the pneumatic lift units.

The figure following illustrates the Air Jet apparatus.

Description of the Apparatus:

1: Compressed air inlet with pressure = 27 psig
temperature = 65°F to 75°F
dew point = -35°F to - 45°F

2: 1/4" Needle valve

3: 1/4" Steel nipple

4: 1/4" x 1/2" Steel

5: 1/2" Solenoid valve - Skinner Electric Valve Div. Conn., 115 volts, 60~, 8 watts, 150 psi. Valve #LC2DB4150, normally closed.

6: Universal timer - Dimco Gray Co.

7: 1/2" steel nipple

8: 1/2" x 3/4" steel bushing

9: Flowmeter - Fischer & Porter Co. #6111 A329 3B1. Precision bore florator tube #FP-3/4-27-G-10

10: 3/4" x 1/2" steel bushing

11: 1/2" iron nipple length = 1"

12: 1/2" Globe valve

13: 1/2" x 3/8" steel bushing

14: Imperial brass hose connector - connecting 3/8" bushing with 1/2" plastic tubing

15: 1/2" I.D. flexible plastic tubing length = 40"

16: 1/4" steel pipe length = 2"

17: 0 to 30# pressure gauge

18: 1/4" steel tee

19: 1/4" x 1/4" half union coupling, Imperial

20: 1/4" copper tubing

21: 1/4" nut, Imperial

22: 1/4" x 1/4" half union coupling, Imperial

23: 1/4" x 1/4" steel coupling

24: 1/4" x 1/4" hose connection, Imperial Brass

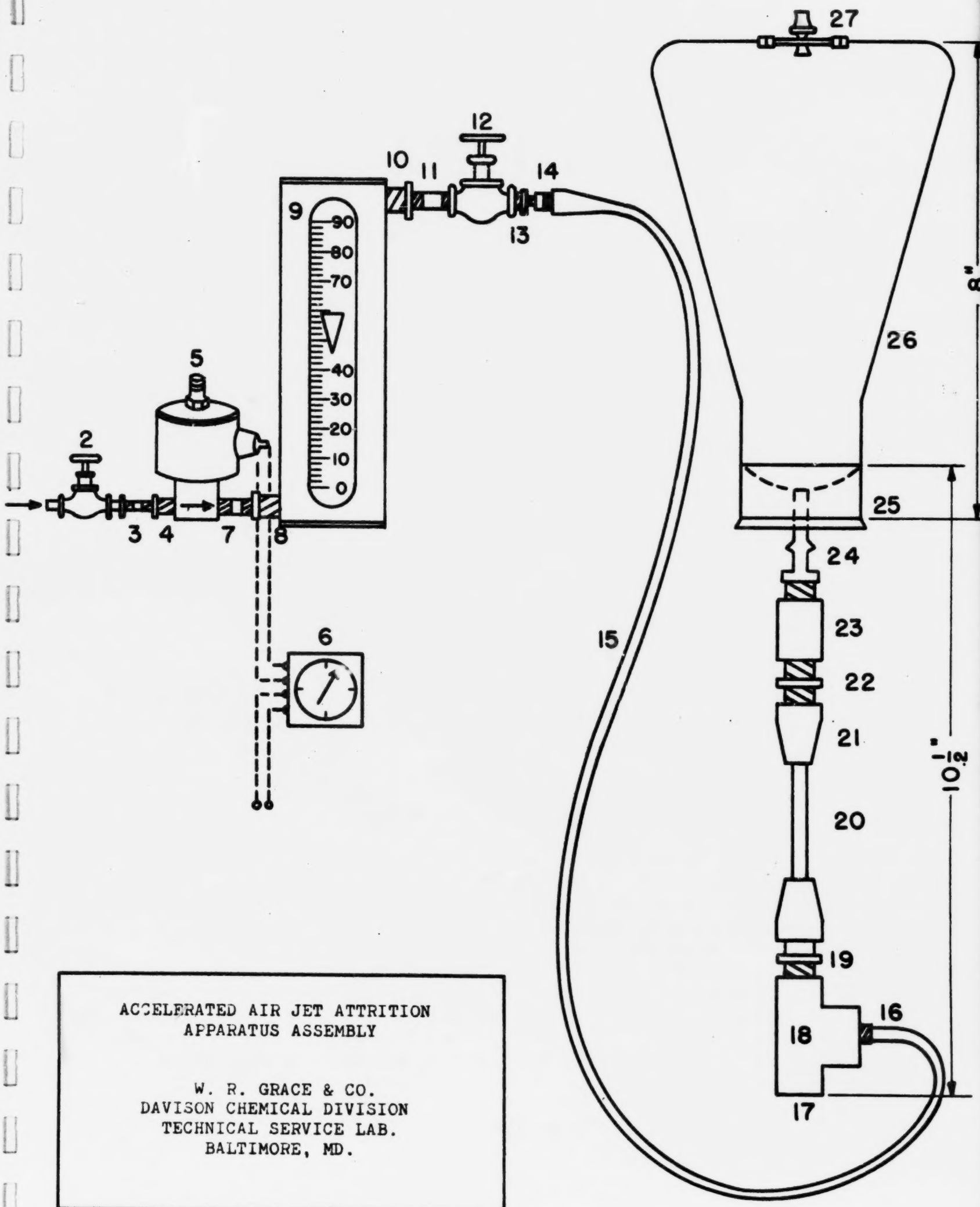
25: Rubber stopper No. 9 Neoprene, concave surface 7/16" deep

26: 1000 ml conical flask with 1" hole in bottom, Pyrex No. 4984

27: No. 20 mesh support screens (upper - 2 1/2" x 2 1/2", lower 1 3/4" x 1 3/4") bolted into position

Working Principle:

Dry air is admitted for a given period of time, through a concave stopper at a certain flow rate. The particles of preweighed sample are caused to rub against each other and against the sides of the container by the air flow. At the end of test, the material is rescreened on #16 mesh screen and the retained material is weighed. The ratio of weight lost divided by the original weight, multiplied by 100, equals the percent weight loss or attrition loss.



ACCELERATED AIR JET ATTRITION
APPARATUS ASSEMBLY

W. R. GRACE & CO.
DAVISON CHEMICAL DIVISION
TECHNICAL SERVICE LAB.
BALTIMORE, MD.

Established Conditions for Testing Alkalized Alumina Beads with the Following Properties:

Shape	Spherical
Size	8 to 14 Mesh
Average Bulk Density	40 to 50 lbs./cu.ft.
Total Volatile at 300°F	2.0%

Testing Conditions:

Degree of Severity	Ist	IInd	IIIrd
Rotameter Reading, %	26	30	35
Volumetric Flow Rate in S.C.F.M.	3.0	3.55	4.25
Time in Hours	2.5	1	0.5
Screen Mesh	14	14	14

All attrition losses for I, II, and III degree are reported for an average time of 1/2 hour.

Standard Procedure for IIIrd Degree Severity for Alkalized Alumina Beads:

A 30 gram sorbent sample (± 0.1 gram) previously screened on a No. 14 U. S. Standard Screen is placed in an inverted one liter conical flask (26). The flask has a one-inch hole centered in its bottom which is covered by a 14 mesh screen. Dry air (-40°F D.P.) is admitted for 1/2 hour through a concave stopper at 4.25 S.C.F.M. flow rate. At the end of 1/2 hour, the material is rescreened on a U. S. #14 mesh screen and the retained material is weighed (X grams). Attrition values are calculated as follows:

Let X grams equal the material retained on #14 mesh screen after attrition, then

$$\frac{30 - X}{30} \times 100 = \% \text{ attrition loss}$$

The same procedure is followed for Ist and IInd Degree Severity tests except that a time of 2 1/2 hours is used for Ist degree, and 1 hour for IInd degree. However, the attrition loss is reported on an average time of 1/2 hour. Results in a given piece of apparatus have generally been reproducible within a maximum deviation of ± 10% of test results.

A typical result of % attrition loss of the standard alkalized alumina has been reported in Table #1.

TABLE I

Standard Alkalized Alumina	% Attrition Loss Converted to ½ hr. Basis
Ist Degree of Severity	8
IInd Degree of Severity	11
IIIrd Degree of Severity	15

Factors Affecting A.A.J.A.

The following factors are known to influence the test results:

a. Flask and stopper configuration

b. Sorbent moisture content and air moisture content

c. Air rate - the rate must be controlled by a pressure regulator large enough to damp out any pressure surges in the air supply.

d. Air inlet pressure has been found to be a factor as well as air rate.

Three Degrees of Severity

The attrition loss has been found to be proportional to the air velocity, "higher the velocity, higher the attrition loss". But the attrition loss is not linearly proportional to air velocity. There appear to be three distinct degrees of attrition as the air velocity is increased. These three distinct regions are called Ist, IInd, and IIIrd degrees of severity.

Ist degree of severity is at a low air velocity and the attrition loss in this case is mainly due to rubbing of particles with one another and with air (low degree of severity).

IInd degree of severity is at medium air velocity and the attrition loss is partly due to rubbing and partly due to impact (medium degree severity).

IIIrd degree of severity is at high air velocity and the attrition loss in this case is mainly due to the impact of particles with the metal screen and glass surface (high degree of severity).

APPENDIX B

Sophisticated 5 Module Field Test Unit

I. Introduction

The alkalized alumina, System II, test unit consists essentially of the following five modular units.

- Reactor Module
- Analyzer Module
- Control Module
- Synthetic Flue Gas Module
- Air Conditioning Module

The first four modules are approximately 2' x 2' x 4'. The smaller air conditioning module provides cooling air for proper operation of the analyzer and control modules when testing in power plants at high ambient temperatures.

The system has been designed to manually or automatically monitor the sorption of SO_2 contained in a flue gas stack over any desired number of cycles of sorption and regeneration of the sorbent. In the event that it is desired to evaluate a synthetic flue gas or alternate reducing gases, provisions have been incorporated for doing so.

II. Description of Modules

The following will serve to describe and indicate the operation of each module:

A. Reactor Module

The reactor module consists of:

- Furnace heated reactor unit large enough to contain one quart of sorbent.

- Syringe pump for controlled water flow, if necessary, into gas being sorbed.

- Vacuum pump for pulling flue gas out of power plant stacks and into and through reactor.

- Primary water cooling and removal trap after sorption.

- Sulfur trap for use during regeneration.

B. Analyzer Module

This module analyzes the flue gas entering or exiting from the reactor and contains the following equipment:

- F & M gas chromatograph.

- Barber Coleman recorder with disc-integrator.

- Two gas sampling valves; one of 5cc capacity for SO_2 analysis and the other of 1cc for H_2S analysis.

- Thermoelectric cooler having two cells for continuous use in removing water from gas prior to entering the chromatograph column.

C. Controller Module

This unit contains all of the necessary devices for setting and monitoring the condition of a run.

- Timing clocks to set the automatic timing for the following functions:

  - Sorption

  - Purge #1

  - Regeneration

  - Purge #2

- Gas sampling
- Furnace controller
- 12 point Barber Coleman recorder for monitoring the various heated portions of the systems.
- Fischer Porter flow recorder for monitoring the flue gas flow.
- Switches to enable the choice to be made between automatic or manual operation.

D. Synthetic Flue Gas Module

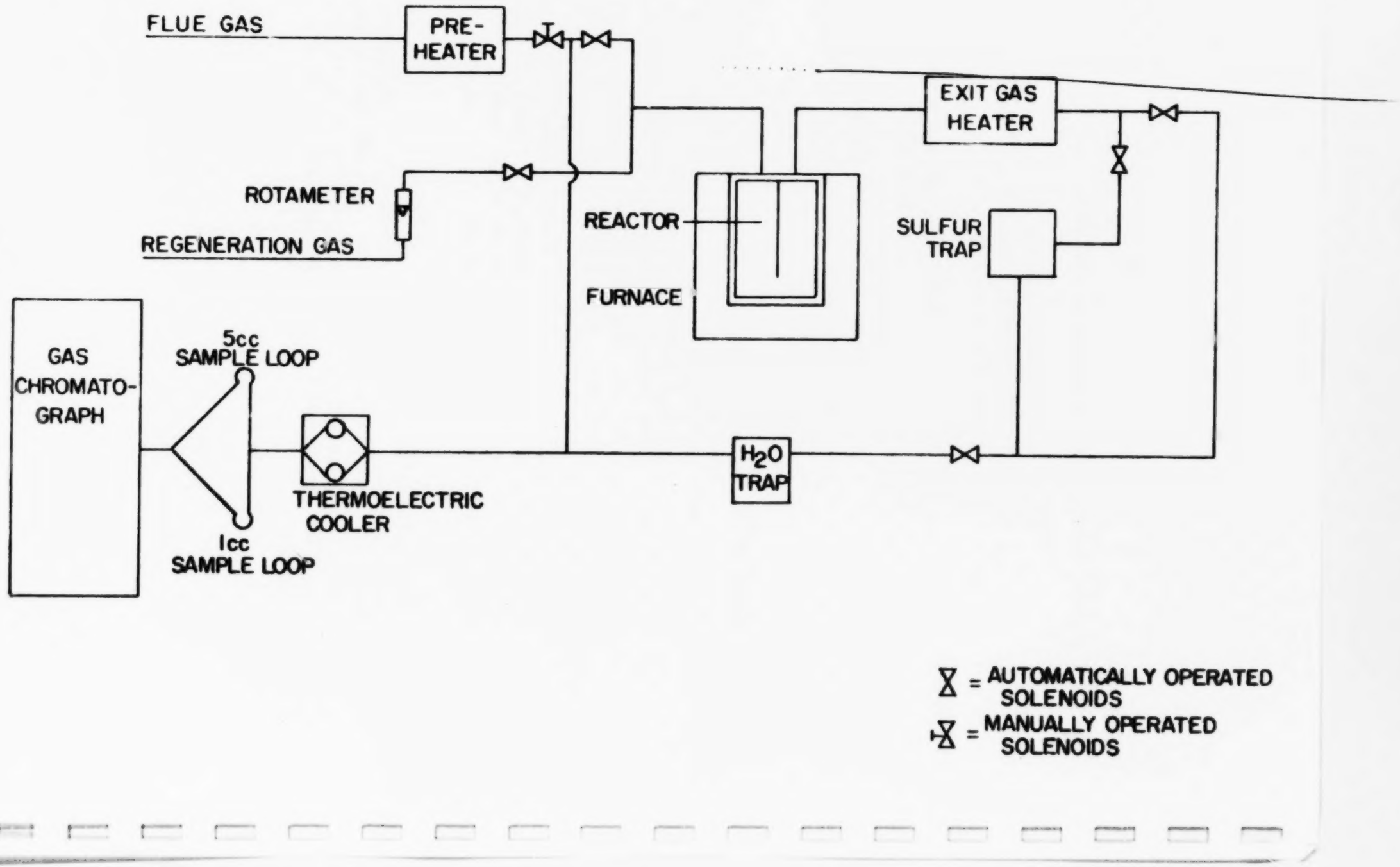
This module contains the necessary devices such as flowmeters and piping connections to permit the make-up of a synthetic flue gas or the study of other reducing gases. It also supplies the CO_2 required for purging of the system operation of certain valves during automatic operation of the system.

An air compressor is also located in this module and serves to provide the necessary air to the reactor for rapid cool down prior to the sorption portion of the cycle.

E. Air Conditioning Module

This unit supplies cooling air to both the analyzer and control module to insure these delicate parts against excessive heat such as is encountered in many power plant locations.

FLUE GAS ADSORPTION FLOW DIAGRAM



APPENDIX C

W. R. GRACE & CO.

Development of Improved Alkalized Alumina for SO_2 Control

Organization Chart

Project Director: N. E. Miller

	Phase I	Phase II	Phase III
Principal Investigator:	W. S. Briggs	E. Eichhorn	P. K. Maher
Senior Scientist:	T. Cheavens	L. Baral J. Pryor A. Zimmer	H. Lee
Chemists & Chemical Engineers:	D. Wallace D. Henderson	A. Lengade	J. Pilato

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